Progress in Energy and Combustion Science 38 (2012) 113–137

Contents lists available at SciVerse ScienceDirect

Progress in Energy and Combustion Science

journal homepage: www.elsevier.com/locate/pecs

Review

Pollutants from the combustion of solid biomass fuels

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ARTICLE INFO

Article history:
Received 26 July 2010
Accepted 25 July 2011
Available online 25 November 2011

Keywords:
Biomass
Combustion
Pollutants
Modelling

ABSTRACT

This review considers the pollutants formed by the combustion of solid biomass fuels. The availability and potential use of solid biofuels is first discussed. This is followed by the methods used for characterisation of biomass and their classification. The various steps in the combustion mechanisms are given together with a compilation of the kinetic data. The chemical mechanisms for the formation of the pollutants: NOx, smoke and unburned hydrocarbons, SOx, Cl compounds, and particulate metal aerosols are outlined. Examples are given of emission levels of NOx and particulates from combustion in fixed bed combustion, fluidised bed combustion and pulverised biomass combustion and co-firing. Modelling methods for pollutants are outlined. The consequential issues arising from the wide scale use of biomass and future trends are then discussed.

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doi:10.1016/j.pecs.2011.10.001

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Nomenclature

A	Pre-exponential factor for devolatilisation
A_p	Surface area of the particle
A_i	Pre-exponential factor
B	Biot Number
C_g	Reacting gas species concentration in the bulk gas
C_1	Experimentally obtained diffusion coefficient
C_{pM}	Specific heat of moisture
D_o	Bulk diffusion rate coefficient
d_p	Particle diameter
E	Activation energy for devolatilisation
E_i	Activation energy for the intrinsic reactivity
f	Xm/M
ΔH_M	Enthalpy of vaporisation of moisture
k_{eff}	Effective rate constant
kgas	Thermal conductivity gas
ksolid	Thermal conductivity, solid
M	Initial moisture content
m_p	Particle mass
N	Dimensionless particle reaction order
Nu	Nusselt Number
P_{ox}	Partial pressure of the oxidant species in the surrounding gas
R	Process rate
R_c	Rc is the chemical kinetic reaction rate constant
T_p	Particle temperature
T_∞	Bulk gas temperature
T_{evap}	Evaporation temperature
t	Time
V	Volatile matter, non-dimensionalised
U	Fractional burnout
X_M	Current moisture content
α	Constant, relates current particle diameter to the degree of burnout
η	Effectiveness factor
ρ_M	Density of moisture

Acronym list

ASME	American Society of Mechanical Engineers
BET	Brunauer, Emmett and Teller Method
CEN	Comité Européen de Normalisation
BS	British Standard
CFD	Computational Fluid Dynamics
CCN	Cloud condensation nuclei
daf	Dry ash free
D-P	Dubanin-Polyani (Method Surface Area Measurement)
D-R	Dubanin-Rabinovich (Method of)
EC	Elemental Carbon
FTIR	Fourier Transform Infra-Red
ISO	International Organisation for Standardization
LES	Large Eddy Simulation
OC	Organic carbon
PAH	Polyaromatic Hydrocarbon (Poly-Aromatic Hydrocarbon)
pf	Pulverised Fuel
PM1	particulate matter less than 1 μm in diameter
PM10	particulate matter less than 10 μm in diameter
PY-GC-MS	Pyrolysis-Gas Chromatograph-Mass Spectrometer
PKE	Palm Kernel Extruder
RANS	Reynolds-Averaged Navier Stokes
RCG	Reed Canary Grass
SRC	Short Rotation Willow Coppice
SW	Switch Grass
TGA	Thermal Gravimetric Analyser
toe	Tons Oil Equivalent
UBC	Unburned Carbon
VM	Volatile Matter

Subscripts

th	Thermal
e	electrical

1. Introduction

1.1. The role of biomass combustion

This review is concerned with the combustion of solid biomass fuels, either directly, or with minimal pre-processing, as a primary energy source and the resultant environmental pollution. There is an expanding market in the use of biomass for supplying both transport fuels and electricity/heat. In the former case, the interest is in producing derived liquid biofuels for transportation purposes via first or second generation processing technologies [1] i.e. produced by physical, biological (fermentation), chemical or thermal processing. For electricity and heat generation, solid biomass fuels are the main contenders. Consequently, there are pressures on supply to different sectors from a resource point of view. Some of these pressures are discussed briefly here, although a number of reviews have considered the utilisation and environmental aspects of different generation technologies [1–3].

Solid biomass covers a wide range of materials: woods, straws, agricultural residues, processing wastes, algae and seaweeds. Strictly it does not include peat which is partially decayed plant matter, manures, meat by-products and other waste foods. The early use of biomass was based on easy accessibility and availability, but the use decreased in many countries due to shortages in the

19th Century and by the emergence of fossil fuels. Biomass is still widely used in Developing Countries because it is cheap and easily available. In addition, the application technology is simple and the feedstock needs little in the way of processing, hence its popularity especially in countries with considerable reserves of biomass [4–9], despite major efforts to make available other technologies such as solar cookers. As is the case with conventional fuels, extensive compilations or data bases on the properties have been developed [eg [2,9–12]].

Today, there is renewed interest in many industrialised countries in biomass combustion, especially bio-heat, and, in Europe, co-firing. Older technologies for bio-heat [eg [13–15]] are still widely employed but are now moving to a more advanced stage in many industrialised countries [eg [16–18]]. This is a result of environmental and climate change concerns, and because of security of energy supplies in a world where fossil fuels are concentrated in a few countries, and resources finite. Of the alternative renewable supplies biomass has the advantages that it is geographically widely available and it is a storable energy. While biomass possesses the advantage of CO_2 neutrality, or nearly so, there are potential problems concerned with the environmental pollution that it causes and the influence on food production. In many of the small combustion appliances there is significant atmospheric pollution - indeed it is estimated that many millions of people are exposed to the effects of wood smoke and 1.6 million people/annum die as a result of pollution [19–22]. Biomass feedstock expansion can have adverse impacts on the environment; particularly where there has been a major change of land-use (such as deforestation) when there can be little or no saving in Greenhouse Gas emissions. In this respect, economic and life cycle analyses are helpful. These can identify the benefit, if at all, of various strategies, but they are sensitive to the weightings set to the pollutants and particularly to carbon dioxide and the other greenhouse gases such as CH_4 and N_2O [eg [23–25]].

1.2. Availability of biomass

Many estimates have been made of the possible contribution of biomass to future energy supply, especially in the next 30–50 years. Biomass energy annual usage currently represents approximately 8–14% of the world final energy consumption as detailed in Table 1.

The data in this Table come from a number of sources [2–8,26–30]. Current and future estimates of biomass utilisation are subject to uncertainty and global values can vary by a factor of 5 [4–8] but well-resourced information is available for major countries such as the US, Europe, Russia, China, India and Brazil. The upper estimate of biomass annual availability [29] is about 4500EJ (220Gt mass, 108 Gtoe)[1EJ = 24Mtoe] and is almost ten times the world current energy requirement. Resources vary from country to country and are dependent on geographic location, the climate, the population density and the degree of industrialisation of the country.

Table 1
Annual global energy consumption Gtoe, 2010 [2–8, 26–31].

Fossil Fuels	**10.45**
Oil	4.03
Coal	3.56
Natural Gas	2.86
Nuclear	**0.63**
Renewables	**0.94**
Hydro	0.78
Wind, commercial biomass, solar	0.16
Estimated biomass (traditional)	1–2
Total global energy consumption	**12.00** Gtoe commercial energy, or 13.0–14.0Gtoe including all biomass

Essentially biomass used as a fuel can be divided into the following two major groups [7]:

(1) Biomass, grown directly for use as a primary fuel,
(2) Traditional bioenergy (e.g. biomass for cooking),

The amount of the former has been estimated [7] as 6 EJ [144 Mtoe] and listed under “Renewables” in Table 1, and the latter as39EJ (936 Mtoe). This gives a total of 45EJ [1080Mtoe] as indicated in Table 1, although some estimates make it slightly greater. Since the net global production of biomass is estimated as 2280EJ/yr, so the percentage of the biomass used for fuel is 2%. Food production on the other hand is equivalent to about 273 EJ/yr i.e. approximately 12%.

Predictions on the future usage of biomass are usually to 2050, and indeed some as far as to 2100 [6–8,27–31]. It has been concluded that the contribution from biomass could be raised to 200 EJ/year (4.8 Gtoe) by 2050 [6–8,27], but some estimates make it five times greater (24 Gtoe) [27]. Because of the competition of land for bioenergy crops versus food, and because of the sustainability requirement, there are advantages in integrated processes, where the primary value products, foodstuffs and oils are produced, and the agricultural residues and biomass wastes are used for energy applications.

There have been many studies of biomass sustainability for various regions of the world [eg [29–31]]. Scrutiny is required with respect to deforestation to make way for crops, as has been the case with palm oil; and with respect to the production of feedstocks (e.g. wheat and maize) for liquid biofuels, where there is direct competition with food production, and where large inputs are required in crop production. These types of problems have implications for solid biomass production also. For instance in Europe [25,29], managed forests dominate the landscape in the north, and arable land in other parts. Conservative estimates suggest a total bioenergy potential from agriculture, forestry and waste of almost 300 Mtoe in 2030. Of this 142 Mtoe will come from agriculture alone. This is equivalent to 12% of the utilised agricultural area in 2030. While the improvement of food production techniques could release a significant amount of land for fuel production, there is interplay between the provision of liquid biofuels, solid biomass and food although, at present, greater attention has been devoted to the former [31].

The development of an international traded market in a similar way to coal and oil is vital [32], but in the case of biomass, certified sustainable sources and a legislative framework to control sustainable supply are also required. However other issues are raised, such as safety and the prevention of the migration of pests.

Finally, the fate of the nutrients in the biomass is an important factor in its sustainability and utilisation. In some applications the biomass nutrients, potassium or phosphorous, can be recycled by returning ash back to the soil. But the nitrogen compounds cannot easily be recycled in this way even though they are often a major input into fuel production. None of the nutrients can be recycled if biomass is co-fired with coal.

2. Combustion of solid biomass fuels

As will be shown during this review, the scale of a combustion unit, as well as the biomass type and properties, have important impacts in terms of the pollution produced. Therefore, this section will give an overview of combustion equipment, and biomass types and their combustion characterisation.

2.1. Methods of utilisation of biomass

A variety of methods of utilisation are possible for biomass which evolved from the technologies developed for the combustion of the solid fuels, coal and coke. These are described in standard text books on fuel technology and combustion engineering [33–42]. In some cases, biomass is burned in equipment designed for coal firing, with only slight modification, and this influences the pollutants formed. The methods available are open fires (up to $3kW_{th}$), simple stoves, Patsari cookers and household heating (1–10 kW_{th}), fixed bed combustors (up to 5 MW_{th}), moving or travelling grate (up to 100 MW_{th}), fluid bed (up to 500 MW_{th}) and pf/suspension firing/and co-firing (up to 900 MW_{th}). All combustion applications have the potential to release airborne pollutants: methane and volatile organic compounds (VOC); nitrogen oxides; sulphur oxides; hydrogen chloride; polyaromatic hydrocarbons (PAH); furans and dioxins; as well as organic and inorganic aerosol particulate. This review will concentrate mainly on the formation of the airborne pollutants.

Large coal-fired power stations can be a major user of solid biomass fuels. Typically a large (4 GW_e) power station could have a biomass co-firing facility with a total renewable capacity of 800 MW_{th} or more. The advantage of using this form of power generation is the high generation cycle efficiency, extensive emission control equipment and therefore reduced emissions per unit of electricity.

Different biomass particle sizes are required for these different systems, which in turn, impinge on the fuel supply and processing capabilities. For pf (suspended) systems biomass fuel particles are normally reduced to a wide range of 10 μm–1000 μm or more in an attempt to ensure complete burnout in only a few seconds of residence time in the combustion chamber. For fluidized bed systems, biomass fuels are pelletised or chipped to 2–5 mm or larger which satisfy the fluidization requirements. For packed-beds biomass fuels are fired either as received or with minimum preprocessing and the size ranges are much wider, from 5 to 100 mm or even higher for logs (up to 50 cm).

There is another major source of pollution arising from biomass combustion resulting from the deliberate, in-field, large-scale combustion of agricultural wastes. However, by far the largest source of pollution are the emissions from forest fires or grasslands caused by natural phenomena, or by deliberate means, in order to clear forests for agricultural purposes. There have been extensive studies and reviews published of the widespread effects of forest, grassland and agricultural waste fires [eg [19–22,42–45]]. Detailed information is extremely difficult to obtain because of the transient nature of these phenomena and their scale. However some information is available on the emission factors [44,45]. Peat (although not classified as biomass) is also responsible for significant fires, which can be long term, very large in size and can cause considerable air pollution [46].

2.2. Forms of solid biomass fuels

Solid biomass fuels are available in a variety of forms. These include the traditionally available logs and straws, and also processed products such as chips, pellets and pulverised fuels mainly from wood, straw and a range of agricultural residues. Many of the traded biomass conform to standards (e.g. woodchips and pellets via CEN/TS 14961: 2005 (E)) with respect to dimensions, moisture content, ash and nitrogen. In pellet making small particles (2–5 mm) of the biomass are compressed whilst steam heated and the lignin acts as a binding agent [18,47–50]. Alternatively a binder may be added. Pellets are now an accepted form of fuel for many smaller units and are becoming widely used and internationally traded [18,32]. This also means that there are a variety of, often bespoke, feeding and storing arrangements.

Fluidised bed and travelling bed equipment will take larger particles thus minimising the amount of energy required for processing. Power stations require a fuel pulverised to a size similar to that of pulverised coal in order to achieve a high combustion intensity required by their design. Direct firing of pulverised biomass or the co-firing [51–55] with coal requires particles that are ground to less than 1 mm in size which presents a problem with fibrous biomass, and is difficult and expensive (in terms of energy and money). Fibrous biomass requires about 5 times the energy of bituminous coal, however the process of torrefaction [56–60] can modify the nature of the products making it easier to mill [11,50]. Agricultural process residues including nut products, such as Palm Kernel Expeller (PKE), and olive waste are available in ground form and are less fibrous than woods and grasses. The contrast between these different fuels - the fibrous materials - wood (SRC, short rotation willow coppice) and straw, and the easily ground fuels, olive waste and PKE, is shown in Fig. 1. [61].

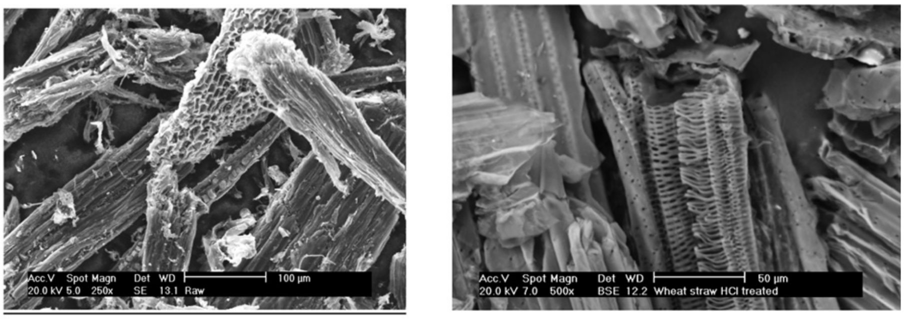
2.3. Types of solid biomass fuels and their classification

Conventional solid fossil fuels are classified by a range of standard tests, which are determined by a number of considerations. Commercially, the ‘value’ of a fuel as determined by calorific value, volatiles, ash content and similar parameters is important, as are safety considerations (flammability characteristics). Technically there are other criteria that determine the mode or ease of transportation or ease/efficiency of use in the end application (e.g. density, hardness, particle size). Finally, environmental factors (S, N contents) are also important.

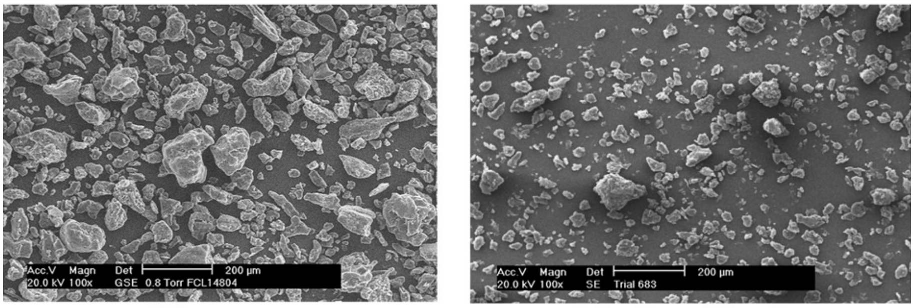
Until recently solid biomass fuels were not traded on a large scale commercially and apart from specialist applications of industrial waste from sugar cane bagasse, palm olive and from paper manufacture. Most of the applications were for domestic heating and cooking. The development in the last decade of biomass on a large industrial scale has prompted the use of standard test methods and in the case of solid fuels the methods developed for coal coking and combustion were used in the first instance. Many of these were based on the existing methods for solid fuels, such as the international standards by ASME, BS, ISO etc [11].

Now the tremendous diversity of biomass feedstock is recognised, there is a need for a comprehensive classification system which covers both physical and chemical specifications and could allow the user to predict the behaviour of a biomass feedstock, via correlations with results from a few simple fuel characterisation tests. Some properties which might be useful to predict include: storage potential; self-heating potential; milling behaviour; pyrolysis behaviour; tar yield; volatile composition; yield and composition of the char and its reactivity towards oxygen; impact of inorganic composition (more variable for biomass compared to coal), on ash behaviour.

Biomass material can be broadly classified into groups based on the general assessment of their source. The resultant major groups, shown in Table 2, are (1) woody: pine chips, an energy crop, willow, (ii) herbaceous: two energy crops are listed - Miscanthus and Switch Grass, (iii) agricultural residues: wheat straw, rice husks, palm kernel expeller, baggasse (a sugar cane residue), olive residue or olive cake (the waste from olive oil mills). Animal wastes such as cow dung form another category although these are not strictly biomass. Data for lignin and cellulose are given in the Table 2 for comparative purposes (the latter is an exact quantity but the value for lignin depends on the type). This broad classification is shown in Table 2 together with analyses.


Acc.V Spot Magn Det WD 100 μm
20.0 kV 5.0 250x SE 13.1 Raw
Acc.V Spot Magn Det WD 50 μm
20.0 kV 7.0 500x BSE 12.2 Wheat straw HCl treated

Willow SRC Wheat straw



Olive waste Palm Kernel Expeller

Fig. 1. Electron microscope photographs of typical biomass fuels, from [61] and unpublished work.

The properties (chemical and physical) of biomass in each of these categories fall over a broad range and it is quite clear that category alone cannot be used as a means of predicting behaviour. There is some suggestion that they can be used to indicate a tendency to form certain types of pollutants, e.g. smoke (from the lignin content as discussed later), and NOx, but much will depend on the combustion environment also.

All biomass contains the nutrients N, P and K and the other major essential elements Ca, Mg, Na and Si. Minor species include Mn, Fe, Mo, Cu, and Zn and the concentrations of all inorganics are dependent on the growing conditions and harvesting time. The amount of chlorine in biomass, particularly straw, is also influenced in the same way, but is often affected by exposure to rainfall, the proximity of sea, or by road transport on salt-treated roads in winter. Inorganics in biomass have been studied extensively because of their significant influence on slagging, fouling, corrosion as well as pollutant formation (eg references [52,53]). The single most important species is potassium [62–66]. Straw would contain typically large amounts of K/Cl: 0.2–0.97 dry% Cl and 0.7–1.3% K; whilst woods would contain smaller amounts of K/Cl: typically <0.1% Cl and 0.2–0.5 %K. Silica tends to be a main component in the ash of herbaceous crops and residues (straws as well as rice husks), while calcium is higher in woods and some of the herbaceous energy crops. This influences the nature of the emitted fine particulates.

Another approach to classifying biomass towards pyrolysis has been the consideration of the main biochemical components, cellulose, hemicellulose and lignin. Here it is assumed that that the biomass thermal behaviour can be predicted from the addition of the pure component behaviours (i.e. they behave independently) [62,67]. This type of classification is shown in Fig. 2. It is also suggested, that in the absence of catalytic species, higher lignin biomass might have higher soot formation tendency, because of its propensity for the production of phenolic tars, which can participate in the soot-forming mechanism. Such a system can be used to classify lignocellulosic biomass, [67] but as shown in Fig. 3, it is

Table 2
Typical proximate (ar, %) and ultimate analyses %(non-aqueous, daf) and (higher heating) calorific values for a range of biomass types.

Fuel	Proximate analysis, ar				Ultimate analysis, daf				S	Cl	HHV
(Oven dried)	Moisture	VM	FC	Ash	C	H	O	N			MJ/kg (dry)
Wood pine chips	4.0	81.3	14.6	0.1	52.0	6.2	41.59	0.12	0.08	0.01	20.23
Willow, SRC	6.96	75.70	16.31	1.03	51.62	5.54	42.42	0.38	0.03	0.01	18.68
Miscanthus giganteus	14.2	70.4	14.1	1.3	49.1	6.4	43.98	0.26	0.13	0.13	19.88
Switch Grass	7.17	73.05	15.16	4.62	49.40	5.70	44.25	0.45	0.1	0.1	17.82
Straw-wheat straw	7.78	68.83	17.09	6.30	49.23	5.78	43.99	0.64	0.1	0.26	17.42
Rice husks	9.4	74	13.2	12.8	42.3	6.1	50.56	1.1	0.1	0.04	16.3
Palm PKE	7.60	72.12	16.18	4.10	51.12	7.37	38.21	2.80	0.3	0.2	20.00
Sugar cane bagasse	10.4	76.7	14.7	2.2	49.9	6	43.15	0.4	0.04	0.51	19.47
Olive residue	6.40	65.13	19.27	9.20	54.42	6.82	37.29	1.40	0.05	0.04	19.67
Cow dung	13.9	60.5	11.9	13.7	54.00	6.4	36.7	0.83	0.03	1.0	17.36
Lignin	9.0	73.5	1.5	16	72.0	6.6	21.34	0	0	0	25
Cellulose	4.1	94.0	0.2	1.7	44.4	6.17	49.3	0	0	0	18.6

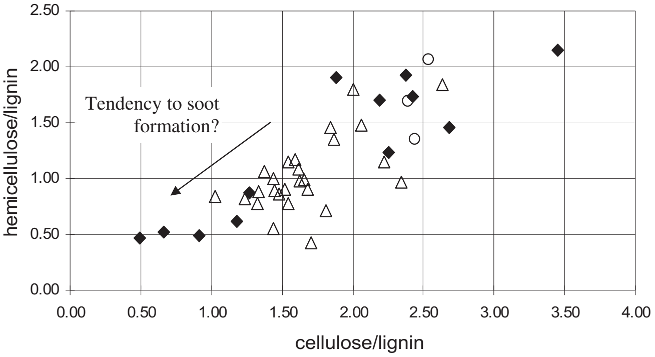


Fig. 2. Possible classification based on cell wall components. ◆ herbaceous; △ woody; ○ miscellaneous residue, [Based on [11,62,65,66,67,68]].

providing the effect of catalyst minerals such as potassium is taken into account [62,64,65]. There is debate as to the reliability of such a system, however, mainly because the influence of all the minerals cannot yet be predicted fully [65]. Potassium has a considerable effect on the pyrolysis mechanism, as does sodium [63–65], and there results a change in the decomposition mechanism, with the alkali metal-influenced reaction producing low tar (primary) products, and higher gas and char yields; and thus less luminous flames [65].

2.4. Characterisation by chemical analysis

The simplest method of classification is based on chemical analysis [62,66–68]. A method has been suggested by Chen et al. [62] which parallels the type of approach adopted for early coal classification systems, is based on a van Krevelen diagram (plot of H/C versus O/C atomic ratios (daf)). The premise in this classification is that biomass feedstocks that fall within clusters in the van Krevelen diagram will have similar properties, regardless of their category. This is shown in Fig. 4, where correlation to high heating value is demonstrated.

This type of approach has now been used by a number of research groups [e.g. [35,62,67,68]] and there has been marked success in the prediction of other properties, such as calorific value, [69] and some success in predicting lignin, and other similar quantities [66,67] from such a plot for lignocellulosic biomass. It should be noted that while some properties, such as calorific value correlate extremely well by this approach, other fuel parameters such as volatile matter or fixed carbon correlate less well, because these parameters are strongly influenced by both heating rate and ash content/composition. There is added difficulty in that the analyses vary across different particle size fractions of the heterogeneous biomass samples [70]. Variation is seen between leaf and stem as well as bark [70–73] and the analyses are affected by time of harvest, geographic origin, fertilizer treatment and length of storage. [74–77].

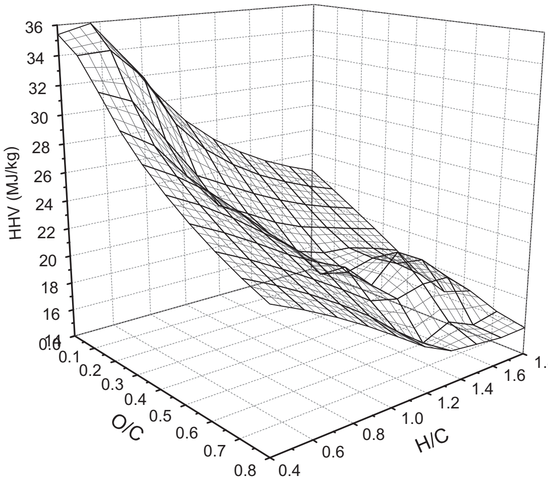


Fig. 4. The van Krevelen diagram for biomass samples. H/C and O/C are the atomic hydrogen-to-carbon ratios (daf, non-aqueous).

2.5. Characterisation by TGA, PY-GC-MS and FTIR

Apart from chemical analysis it is possible to characterise a solid fuel by pyrolysis in an inert gas stream or by combustion. Laboratory scale thermogravimetry in air, yields the burning profile, a mass loss trace and its first derivative, which gives characteristic temperatures for moisture loss, volatile loss, volatile ignition, char ignition and char burn-out. These methods were developed for coal [78] but have been widely used for biomass and some examples are given in Fig. 5. Fig. 5 (a) compares the mass loss curves in temperature programmed combustion for short rotation willow coppice (SRC), wheat straw (WS), reed canary grass (RCG) and switch grass (SW). Fig. 5 (b) displays the first derivatives (burning profiles) for the same biomass materials. It is clear that there are differences between these energy crops and residue. The temperatures at which the maximum burning rates occur is affected

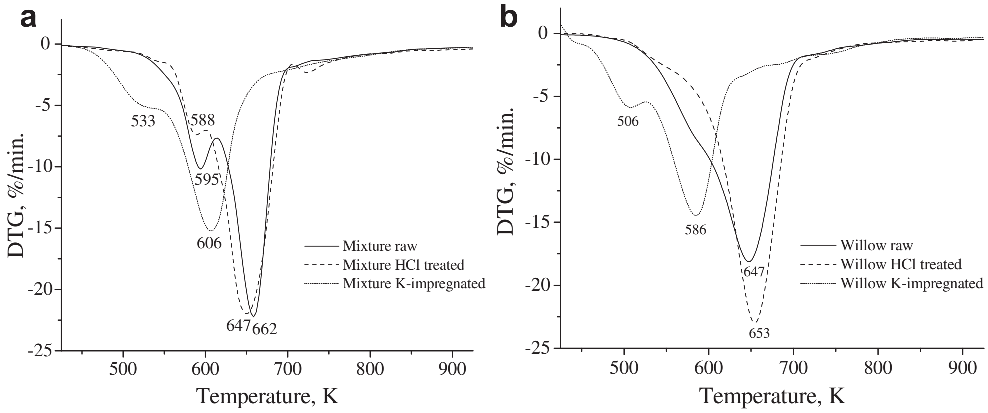


Fig. 3. Differential thermal analysis of (a) “synthetic biomass”, a mixture of lignin, cellulose and xylan; and (b) willow, which had undergone different treatments to remove inherent metals (HCl treated) and to add a catalytic species (eg K-impregnated) [64].

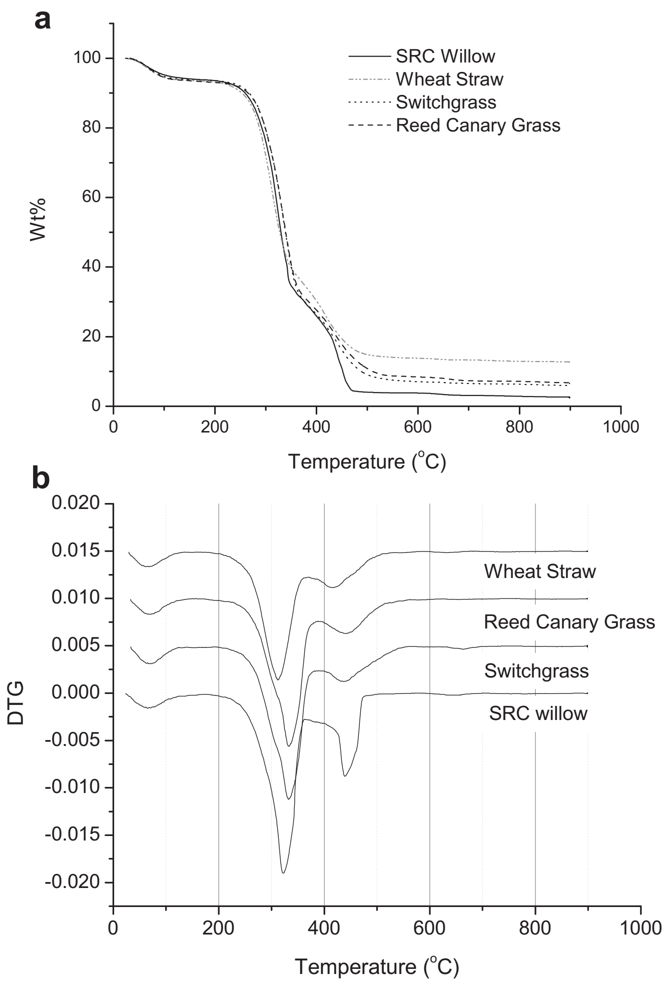


Fig. 5. Burning profiles of three energy crops (short rotation coppice, reed canary grass, switchgrass) and a residue (wheat straw). (a) mass losses as a function of temperature, (b) burning profiles (offset for clarity).

significantly by the alkali metal content of the fuel [64], and these, together with the weight losses during volatile and char combustion regions can provide quantitative information that can used to classify the fuels.

Another method of characterising biomass types is illustrated in Fig. 6 and consists of analytical pyrolysis coupled to a gc-ms [79,80]. This technique yields a fingerprint of tar decomposition products [81–85] which can be traced to the source cell wall component [85].

Considerable advances have been made in the analysis of biomass products but an extremely important but difficult area is in the analysis of high molecular weight tars. They play a major role in the emission of particulate pollutants. New techniques offer considerable opportunities for progress here [79,80].

3. The combustion of solid biomass and the formation of the major pollutants

3.1. General mechanism

Biomass combustion consists of the steps: heating-up; drying; devolatilisation to produce char and volatiles, where the volatiles consist of tars and gases; combustion of the volatiles; combustion of the char.

$$\text{Wet Biomass} \rightarrow \text{heating up/drying} \rightarrow \text{dry biomass} \tag{i}$$

$$\text{Biomass} \rightarrow \text{volatiles (tars and gases)} + \text{char} \tag{ii}$$

$$\text{Volatiles} + \text{air} \rightarrow CO + CO_2\ (+\text{PAH} + \text{unburned hydrocarbons} + \text{soot} + \text{inorganic aerosols}) \tag{iii}$$

$$\text{Char} + \text{air} \rightarrow CO + CO_2 \tag{iv}$$

$$\text{Volatiles (N, S, K, etc)} \rightarrow \text{N, S, K based pollutants} \tag{v}$$

$$\text{Char (N, S, K, etc)} \rightarrow \text{N, S, K based pollutants} \tag{vi}$$

Early predictions of biomass combustion used simplified rate expressions for each of these steps [34–36,86–89], while recent models include more detailed, biomass-specific chemistry to better predict burn-out and pollution formation indicated in Fig. 7. Modelling of each of these steps is discussed in the following sections.

Pollutants are formed alongside the main combustion reactions from the N, S, Cl, K as well as other trace elements contained in the volatiles and char. CO, PAH and soot, together with characteristic smoke markers of biomass combustion such as levoglucosan, guaiacols, phytosterols and substituted syringols [20] are released if the combustion is incomplete, due to factors such as local stoichiometry (mixing), temperature, residence time etc. Thus, the atmospheric emissions can contain tar aerosols and soot, which together with fine char particles and metal-based aerosols such as KCl, form smoke. The nitrogen compounds are partially released with the volatiles, whilst some forms a C-N matrix in the char and is then released during the char combustion stage forming NOx and the NOx precursors, HCN and HNCO. Sulphur is released as SO_2 during both volatile and char combustion. KCl, KOH and other metal containing compounds together the sulphur compounds form a range of gas phase species, which can be released as aerosols, but importantly also deposit in combustion chambers.

The development of models to predict the formation of these pollutants has been a continuing research effort for many decades. Models have been applied to a range of applications and particle sizes, ranging from small pulverised particles less than 1 mm in diameter, to chip, or larger still such as logs, and at the extreme to trees in forest fires. Because of the coupling between chemistry and heat and mass transfer during particle conversion, fuel size has a major effect on the emissions. Although the general features are well understood, there is still debate regarding the relative roles of the controlling mechanisms. Pyrolysis might be controlled by either the chemical kinetic rate or the internal heat transport rate, and char oxidation might be controlled by the chemical kinetic rate or internal or external diffusion rates. The actual rates in the regimes for drying, pyrolysis, char formation and char combustion depend on particle size and can be defined as thermally thin, or thermally thick with thermal wave regimes. In the first case, the temperature is constant across the particle and this is normally assumed in the heating up step for small (pf) particles in the drying and pyrolysis steps. For larger particles, in fluidised or fixed beds, a thermal wave is assumed to pass through the particle, causing sequential drying, pyrolysis, char formation and then combustion. In this situation all the regimes coexist. The thermally thick case is assumed when there is large sized material involved and considerable thermal gradients.

3.2. Particle heating and moisture evaporation

Biomass moisture content plays a significant role in the combustion process. Typically newly cut woods contain up to about

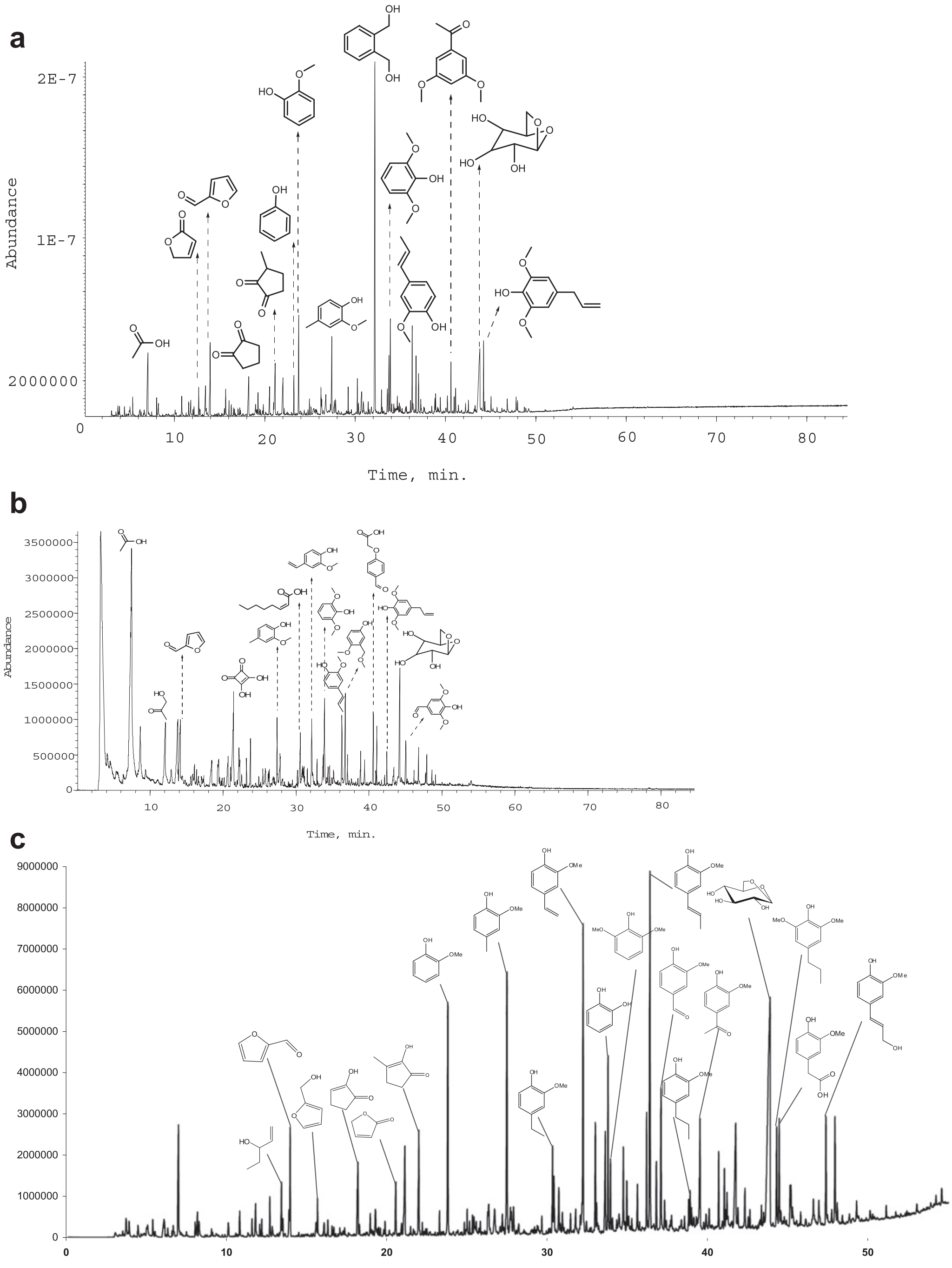


Fig. 6. Py-GC-MS of (a) Miscanthus, (b) Short rotation willow coppice, (c) pine.

50 wt% moisture, present as bound and free water, and even after considerable ambient drying the moisture content is still about 15–20%. For combustion of small particles (e.g. co-firing with pf coal) the particles are assumed to heat up virtually instantly, but there is an efficiency loss due to the latent energy of water evaporation from the biomass. Because of this, and because of the high content of moisture in some biomass, a drying process is usually carried out separately, which significantly affects the temperature and stability of the flame. However in the large-scale utilisation of biomass the drying process is energy intensive and there is industrial interest in using fuels with high moisture contents at one extreme, or pre-processed by using pelletisation or torrefaction at the other, where the use of energy is optimised [11].

Many drying models have been developed, and early models for biomass drying were those used for pulverised coal [90–92], but recently, more detailed models have been developed for larger particles [93–98]. For example, in the case of a small particle it is assumed that the progress of drying is limited by the transport of heat into the particle, and the moisture evaporation rate, $\dot{r}_M$, can be approximated [92] by Eq. (1):

$$\text{If } T_s \geq T_{\text{evap}} \quad \dot{r}_M = f_M \frac{(T_s - T_{evap})\rho_M c_{pM}}{\Delta H_M \delta t}$$

$$\text{if } T_s < T_{\text{evap}} \quad \dot{r}_M = 0 \tag{1}$$

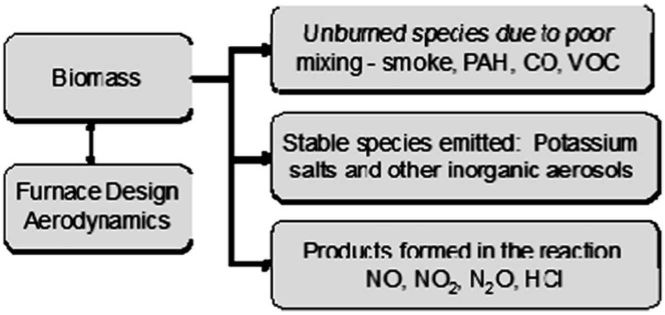

Biomass
Furnace Design Aerodynamics
Unburned species due to poor mixing - smoke, PAH, CO, VOC
Stable species emitted: Potassium salts and other inorganic aerosols
Products formed in the reaction NO, NO$_2$, N$_2$O, HCl

Fig. 7. Diagram of the pollutants formed during biomass combustion.

where $f_M = f_M = X_M/M$. In the case of the drying of small particles, most models, such as that by ANSYS Fluent [99] assume that there is a uniform temperature profiles across the particle. The use of non-uniform temperature profiles is necessary for bed firing and the use of larger particles in fluidized bed and some pf studies [94–98].

3.3. Devolatilisation of biomass

Devolatilisation or thermal pyrolysis occurs in the early stages of combustion of solid biomass and plays an important role, since a large part (typically 80% - see Table 2) of the original biomass is converted to volatile products. Typically the temperature at which pyrolysis starts is about 160–250 °C for biomass fuels compared to about 350 °C for bituminous coal [100–105].

The amount and nature of the pyrolysis products depend on both the final temperature and the heating rate, and are influenced by the size of the biomass particles. Fast heating, under moderate to high temperature, yields more volatiles. High temperatures favour gas production over volatile organics and tars. Thus, in pf biomass combustion, volatiles that are produced during the heating up process crack to form mainly CO, CO_2, H_2O, together CH_4, VOC, H_2 and some trace inorganic products [52,106–114]. While in pf combustion the heavy hydrocarbon content in the biomass volatiles is relatively low, it is more significant in fixed bed and fluid bed combustion systems.

The volatile content of biomass usually contributes about 70% of the heat of biomass combustion which is compared with about 36% for coal volatile combustion. Therefore volatile combustion dominates the biomass combustion processes and char combustion is of less importance in terms of thermal efficiency than it is in the coal combustion. However, the char can still contain up to a third of the energy content of the biomass, and this together with the increasingly more stringent particle emission legislation, makes the prediction of unburned carbon in ash still important. This prediction is difficult for both coal and biomass firing due to the complex behaviour of the 'least easy to burn' fraction, such as the high lignin-containing elements, (e.g. knots in wood and nodes in straw). The additional complexities in the biomass char combustion lies in the high content of inorganic species, which may act as a catalyst or an inhibitor.

Further, factors such as low carbon content, low heating value, and high moisture content of biomass compared with bituminous coal, makes the former difficult to ignite and can lead to problems of flame stability, particularly when burning biomass fuel alone. However, once ignited, the overall burning rate of pulverized biomass fuels is usually considerably higher than that of coal due to the rapid release of volatiles, and high porosity of the biomass char particles. Extensive measurements have been made of the devolatilisation rates and products [103–116] and the kinetics have been summarised in [104].

The reaction rate for the loss of volatiles, V, can be represented by single or multiple order reactions but usually, when modelling combustion, a first order reaction is used, namely

$$dV/dt = k\,[1 - V] \tag{2}$$

$$\text{where } k = A\,e^{-E/RT} \tag{3}$$

A compilation of kinetic measurements over the last decade or so is given in Fig. 8 based on reference [104]. A major issue is whether the single rate holds over the wide range of temperatures encountered in pf, fluid bed and fixed bed combustion. The effects of the potassium concentrations in the biomass on the devolatilisation rate have been studied and kinetics deduced [e.g. [83]]. Effectively, the higher the potassium level the faster the rate of reaction, but up to a limit. Phosphorus, another key plant nutrient, also acts as a catalyst for pyrolysis [84] although it acts as a retardant for the char combustion stage.

As stated earlier a terrestrial solid biomass fuel consists of a combination of cellulose, hemicellulose and lignin. The exact quantities of these species, which can be obtained analytically, determines the processes that take place during combustion from both a physical and chemical point of view [62,110–119]. Many models assume that these three components react independently [103–119] but this may not be the case at higher temperatures when reactive free radicals are rapidly produced.

The devolatilisation models are easily applicable to thermally thin particles where the reaction temperature is constant throughout the sample, but combined heat transfer/pyrolysis models have to be applied to large, e.g. chipped biomass or logs. The defining criterion is based on the Biot Number {Bi = Nu.k(gas)/k(solid)} having a value greater than 1 and typical values for the transition would be particles of about 250 μm diameter [94–98]. A further factor is whether the particles swell or shrink during combustion, since this impacts on the physical and dynamic properties of the particles, which in turn impact combustion behaviour of the char. This is discussed in Section 3.5.

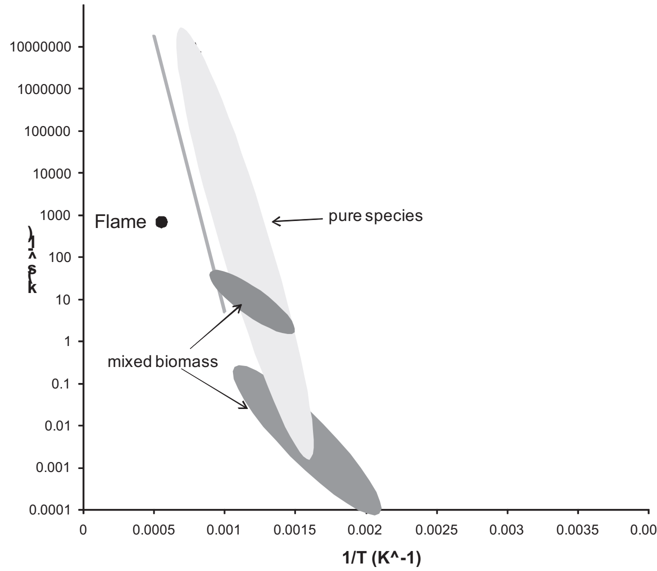


Fig. 8. Comparison of kinetic rates for biomass, where the light grey oval area represents pure cell wall components and the dark grey oval highlights the curves generated by recent present work (demineralised willow) [104]. A point from direct flame data is also shown (●).

3.4. Combustion of the gases and tars

Combustion of volatiles and tars is a key step for the formation and potential emission of VOC, tars, PAH and soot. The composition, and hence calorific value, of the gases, tars and chars derived from biomass depend on the heating rate, final temperature, and mineral (especially potassium) content. The distribution of the trace species such as N, Cl, P and the metals between the gases, the tar and the char is important in relation to their subsequent reaction and formation of pollutants. Unlike coal char, the generated bio-char contains a significant amount of oxygen the amount of which is determined by the final temperature. The oxygen content decreases with an increase in temperature under pyrolysis conditions [120,121] but there is lack of information obtained directly from combustion situations.

A vast amount of experimental data is available on the composition of the major products produced at the laboratory scale and summarized recently by Di Blasi [105] and Klass [121]. Another source is the computed values obtained via the network pyrolysis programs, FG-Biomass [62,122], CPD [100,123] and FlashChain [112]. These models can give information on the gas species, the tars and the composition of the char. Additionally information can be given on the nitrogen partition between the char, tar and gases, important for considering NOx release during combustion.

The composition of the gases, tars and char from wood (willow) pyrolysis calculated by FG-Biomass are shown in Fig. 9. This shows the pyrolysis as a function of the particle temperature but, for this model, there is not much difference in the products as a function of final temperature, most of the final products are produced by about 500 °C and the nitrogen compounds by 800 °C. The products obtained are consistent with experimental results [121] at this temperature. The model does not consider secondary reactions and is validated over a limited range of heating rates and temperatures.

Detailed combustion models are available to calculate the combustion steps of pyrolysis gases [eg [124,125]]. The formation and combustion of tars presents certain difficulties at low temperatures but in high temperature furnaces the tars are rapidly converted to gases and soot. As the temperature rises less tar is formed, little above 1000 °C and none above 1200 °C [126]. Consequently tar formation depends on the application - increasingly significant in fixed bed combustors where relatively low temperatures can be obtained, especially during batch feeding with cold fuel. Di Blasi has summarized the kinetic data available for the decomposition of tars [105].

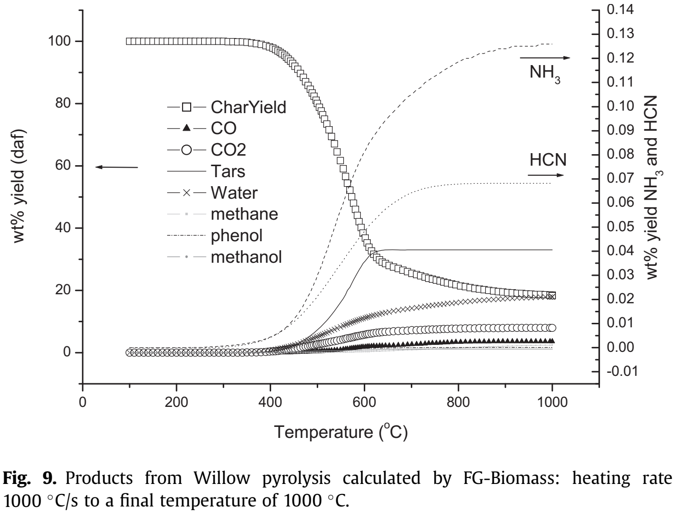


Fig. 9. Products from Willow pyrolysis calculated by FG-Biomass: heating rate 1000 °C/s to a final temperature of 1000 °C.

In summary, the devolatilisation stage provides information on gases, tar and char and it is the combustion of these or their passage through the flame that result in the formation of many of the pollutants. An important part of the combustion mechanism is the formation and reaction of combustion of HCN and NH_3 which is discussed in Section 4.2.

3.5. Char combustion

The chars formed represents about 10–30% of the total biomass by weight but their combustion form important pathways for the release of many pollutants especially nitrogen and many inorganic species. Of course char, or charcoal, can be formed as a separate carbonisation process, and their combustion has been studied for many years [127]. In most combustion furnaces the biomass is directly injected, so all the processes (i)–(vi) occur *in situ*. In thermally-thin particles char combustion occurs after the end of the devolatilization, although in practice a small fraction of char oxidation begins earlier and co-exists with the devolatilisation process. In thermally-thick particles, where a reaction front passes from the external surface to the centre of the particle, the char combustion can be inhibited by the diffusion of escaping volatile products from inside the particle. However, co-existence of devolatilisation and char combustion is observed in practice. Biomass char may contain a significant fraction of the original oxygen and catalytic potassium in the biomass, depending upon the temperature it experiences, thus char combustion behaviour can be significantly different at the temperatures found in fluidised or fixed bed combustion compared to that in pf combustion. Consequently these two cases of char combustion are being considered separately here.

3.5.1. Pulverised biomass combustion

Pulverised biomass char combustion is most applicable in co-firing and the process may typically be expressed as follows:

$$\varphi \mathrm{C(char)} + O_2 \rightarrow 2(\varphi - 1)\mathrm{CO} + (2 - \varphi)\mathrm{CO_2} \qquad \text{(vii)}$$

where φ is the stoichiometric coefficient which is a function of the particle temperature during the combustion. It should be noted that biomass char is not pure carbon as implied by equation (vii). The char combustion process is slower than devolatilization and volatile combustion, and therefore it determines the amount of unburned carbon at the end of the combustion chamber, and, because of the interplay between NOx and carbon-in-ashit also impacts on NOx emission. Although biomass char accounts for a much smaller fraction of biomass fuels, firing large and wet biomass particles in the existing pulverized coal furnace raises concerns over unburned carbon since variations in furnace temperature, flow profiles as well as inter-particle heat transfer may have a significant impact on the combustion of large biomass particles.

The rate of char combustion depends on both the rate of diffusion of the oxygen through the gas boundary-layer around the particle to the reaction sites inside the particle, and by the rate of chemical kinetics of the reaction. Particle dimension and porosity is thus of importance. Char combustion can be modelled relatively accurately using detailed char combustion models, see [eg [34–37,128–140]], which also give details of the extensive other published work in the field for coal chars. In the case of biomass, the burnout rate is more complicated than for coal [133–141] because the char combustion rates are affected by the shape and size of the particles as well as by the composition of the biomass fuel.

Char burnout depends on a number of parameters such as the temperature, char reactivity, particle surface area, oxygen concentration, residence time, ash inhibition and catalytic effects, and the char burning rate can be expressed as:

$$R = f\left(A_p, T_p, \rho_p, p_{ox}, k_{eff}\right) \tag{4}$$

In pf char combustion the char particle is usually considered to be surrounded by a stagnant gas boundary-layer through which the oxygen must diffuse before it comes in contact and reacts with the char. Therefore, the overall oxidation rate of the char may be limited by either the diffusion rate of oxygen to the external surface of the char particle or by the effective char reactivity itself, or by the combination of the two. However, at a high temperature, diffusion is often the limiting process of the char combustion. This is usually expressed as follows:

$$R = R_c\left(C_g - \frac{R}{D_0}\right)^N \tag{5}$$

N is known as the dimensionless particle reaction order [128]. $N = 0$ and 1 are the two typical reaction orders that have been used in the many modelling applications. A zero order of reaction, i.e. $N = 0$ represent a diffusion control surface reaction. In this situation, the knowledge of the bulk diffusivity for the oxidant is the only requirement.

The char combustion rate, (dm_p/dt), for a global reaction order of unity ($N = 1$) can be expressed as

$$\frac{dm_p}{dt} = -A_p p_{ox} \frac{D_0 R_c}{D_0 + R_c} \tag{6}$$

Eq. (6) takes into consideration the effects of both the kinetics and the diffusion.

For pf coal char particles, the diffusion rate coefficient and the chemical kinetic rate constant can be calculated in a way that is commonly used in modelling methods [99], as follows:

$$D_0 = C_1 \frac{\left[\left(T_p + T_\infty\right)/2\right]^{0.75}}{d_p} \tag{7}$$

$$R_c = \eta \frac{d_p}{6} \rho_p A_g \left[A_i e^{-E_i/RT_p}\right]$$

d_p is the particle diameter and assumes the particle is spherical. $\eta$is the effectiveness factor that represents the influence of the pore diffusivity and it can be expressed as a function of parameters such as the concentration of oxidant in the bulk gas, the bulk diffusivity, the porosity, tortuosity and the internal surface area of the char particle. Thus, the chemical kinetic rate R_c is controlled by a combination of the intrinsic reaction rate and the pore diffusion rate.

While char reactivities for coals under pf conditions are relatively well established [128,130,132,142], only a very limited amount of data are available on biomass char burning rates or related data on the char surface area. From Eq. (4) it is seen that information is required on the surface area through the lifetime of the particle, reactivity and the effect of annealing. With biomass some information is available [133–140,143–145] on the reactivity and the surface areas, and it appears that the effect of annealing is small [135]. Little is known about the oxygen reaction order, but it is assumed to be the same as for coal chars [130,131]. It is generally accepted that biomass chars are more reactive than coal char because of the more disordered carbon structure. This is particularly so in the early stages of char conversion, where chars are high in oxygen, see for example, Wornat et al. [135,136] who showed biomass chars are very reactive in the early stages of char conversion and burn almost under diffusion control in high temperature flames. As carbon is consumed this is accompanied by a preferential loss of catalytic elements such as K (volatilises as chloride and hydroxide at high temperatures) and this leads to a reduced reactivity in the biomass chars, see for example [5].

A plot of the intrinsic reactivity for various biomass chars against 1/T is shown in Fig. 10 based on reference [63]. Also, summarised is the data by Smith [128] for a range of carbons including coal chars of $p = 3050 \exp(-179.4/RT)$ kg/m^2 s where R is in kJ/mol. The intrinsic reactivities given by Smith are based on various methods of surface area measurement, including standard BET, approaches using CO_2 adsorption isotherms (273 K, D-R, D-P), as well as CO_2 adsorption at 193 K (and applying the BET isotherm). This may be one of the factors giving rise to the scatter in intrinsic reactivity in the data compiled by Smith, and shown by the dashed lines in Fig. 10 which bound the data.

The results for biomass often include a catalytic influence of metals such as potassium and this is shown in Fig. 10 for potassium. The expectation is that the early stage of char combustion is promoted by the potassium but this is lost by evaporation as the char combustion proceeds, and so the reactivity changes throughout the reaction by a combination of this and by annealing. The annealing effects will not be exactly the same as those shown by coal chars.

More recently, Di Blasi [140] has made a compilation of chemical reaction rates for a range of biomass chars and found values of E between 114 and 230 kJ/mol. The metal contents of these chars were not specified. Surface areas were not given either, and so, in order to compare these with the intrinsic reactivities shown in Fig. 9 these were assumed to be 100 m^2/g, as discussed later.

Unlike coal particles that soften and tend to become spherical, many biomass particles retain their original irregular shape during devolatilisation but it appears to depend on the cellulose and potassium contents. Fig. 11 (a) illustrates the hollow char particle (which has broken open) seen upon the combustion of demineralisation of SRC willow in a flame. Fig. 11 (b) illustrates the type of char seen when 1 wt% K is added to the demineralised willow sample, and then combusted in a flame (as discussed in [65]). The presence of K promotes high char yields with very porous char particles, while the absence of K promotes high tar yields and produces small char yields and char particles with more cenospheric structures. Fig. 12 also illustrates the types of chars produced from different types of biomass [141]. These chars had

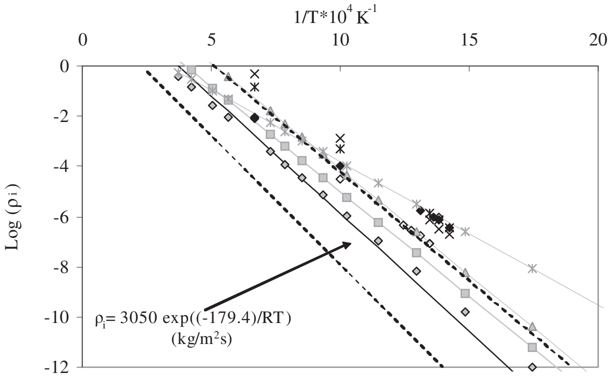


Fig. 10. Intrinsic reactivities (kg/m^2 s) for the untreated and water washed biomass chars taken from [63]: miscanthus (◆), miscanthus water washed (◇), willow coppice (×), willow coppice water washed (*). The equation for intrinsic reactivity derived by Smith [128] (……) as well as the observed experimental scatter (—) is also shown. Also shown by grey lines and symbols are data from Di Blasi [140] (refs cited therein as [85,120,121]).

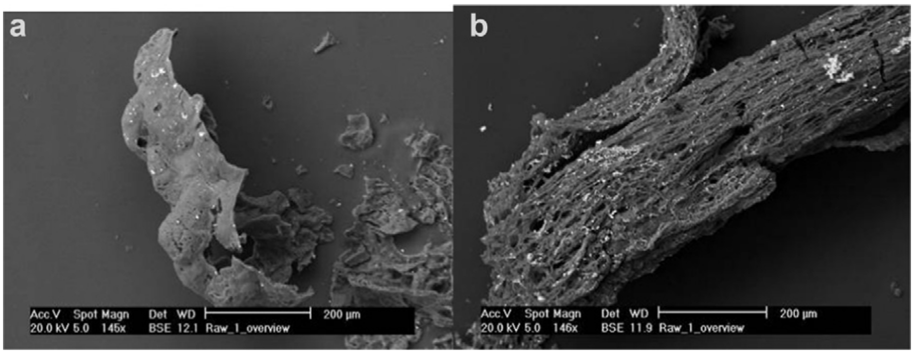

a
b
Acc.V Spot Magn Det WD 200 µm
20.0 kV 5.0 145x BSE 12.1 Raw_1_overview
Acc.V Spot Magn Det WD 200 µm
20.0 kV 5.0 146x BSE 11.9 Raw_1_overview

Fig. 11. Char particles from SRC willow produced from suspended particles in a methane-air flame. (a) Demineralised willow; (b) 1 wt% K-impregnated willow prepared from the demineralise willow used in (a).

BET surface areas ranging from 158 to 277 m^2/g (daf) or CO_2 (D-R) surface areas ranging from 490 to 636 m^2/g (daf). Compare this with coal chars, which have initial CO_2 (D-R) surface areas in the range 175–278 m^2/g [142] and much lower BET surface areas [132]. Also note that char surface areas increase as the coal VM increases from bituminous to low rank coals [142]. Thus, for biomass chars a larger surface area is generated at char combustion which results in a higher oxygen flux into the biomass char particles, and gives rise to much higher char combustion rates. Thus present models are sufficiently accurate to be able predict the rate of burning-out of the char in combustor if the surface area is known.

At the high temperatures that typically occur in a pf combustion furnace, the diffusion is more likely to be the control mechanism of the majority of the char combustion rather than the chemical rate.

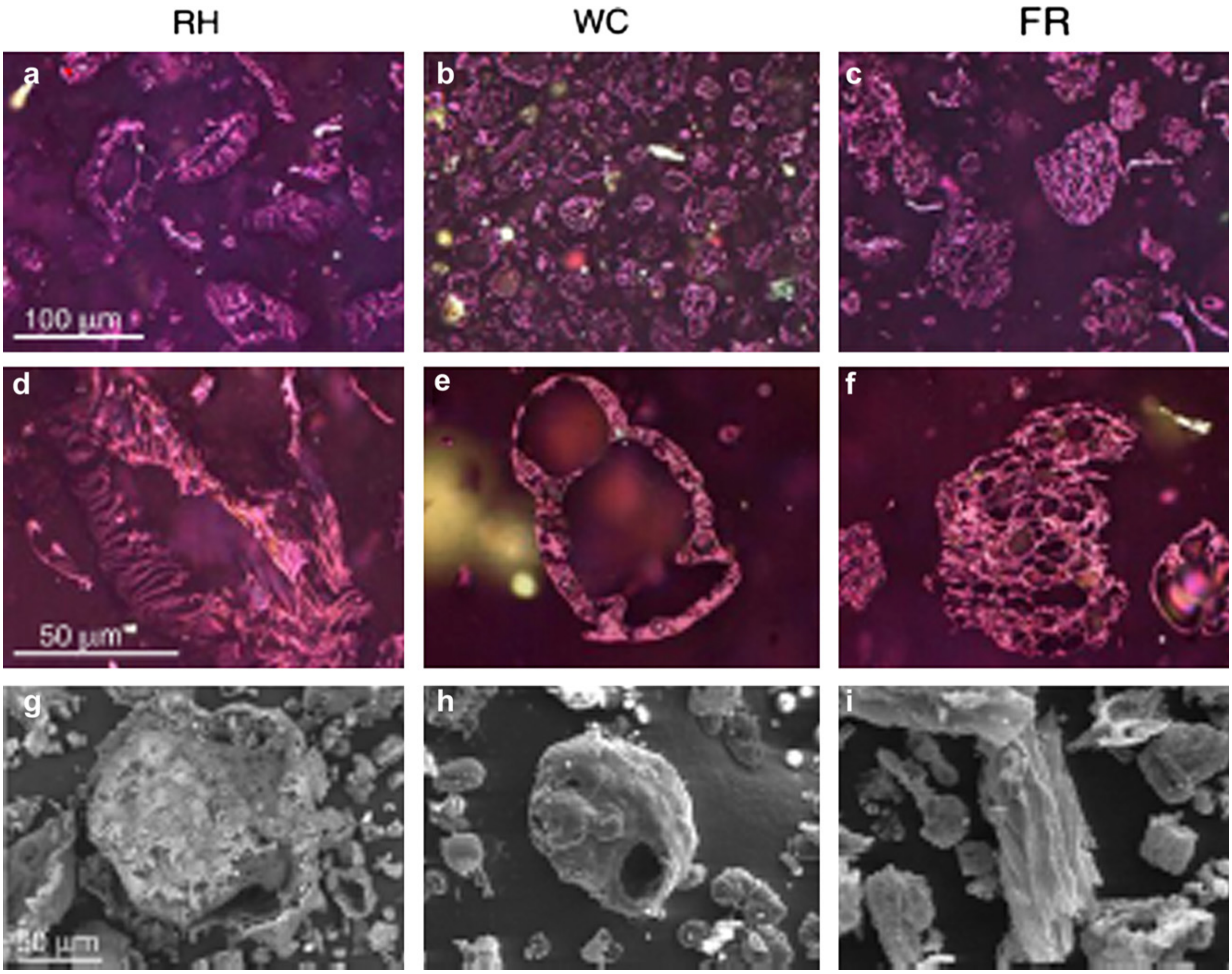


Fig. 12. Appearance of the biomass chars under the optical microscope (top and middle; a–f) and under the scanning electron microscope (SEM; bottom; g–i) showing the typical features of the biomass chars. Rice husk (RH) chars retained a botanical structure (a, d) and show the silica (brighter in the SEM image) associated to the char walls (g). Wood chip (WC) chars were cenospheric (b, e, h) and forest residual (FR) chars had mostly network-like structure (c, f). Optical microscope images were taken under incident polarized light with a 1-λ retarder plate [from [141] with permission].

For biomass particles, large aspect ratios (or minimum to maximum dimension) are usually a typical feature and any shape, from plates, chips or round cylinders to needles and fibres may be present. The immediate effect of this is the increased surface area of the particle compared with the equivalent spherical particle resulting in enhanced diffusion of the oxidant to the pores within the biomass char particles. Note also that the particle size, particle surface area and particle density are changing during combustion. For coal char combustion modelling, the change of particle diameter is usually calculated by specifying a burning mode constant α so that current particle diameter is related to the degree of burnout, for example as follows

$$\frac{d_p}{d_{p,0}} = (1-U)^{\alpha} \tag{8}$$

where$U$ is the fractional burnout and the model constant for coal char usually takes the value of $0 < \alpha < 1/3$. Experimental information is required on how this parameter varies for biomass with the type of char, cenospheric or network.

A more appropriate approach should also account for the variations in the surface areas which can change significantly during char combustion. Fig. 13 illustrates the form of the surface area change of a Pittsburgh 8 coal char particles during pf burnout as predicted by the 'pore tree model' [132]. It is proposed a similar type of function might apply to biomass chars, although there is a dearth of experimental data. The magnitude of the initial surface area depends on the heating rate for char production [146], (and the method of measurement of surface area). Considering the fact that biomass fuels are usually more porous, reactive and contain much higher volatiles than coal, the variations in sizes and surface areas would be significant during combustion. Even with modest assumptions concerning initial char surface area and porosity (say 90 m^2/g by the BET method), the pore-tree model predicts increases in surface area with burn-out, as shown in Fig. 12. In this case, the surface area increases as the reaction progresses to a maximum of 130 m^2/g, with an average value of about 100 m^2/g. Coal char data varies significantly, but the data in Fig. 13 is that from reference [132].

Studies on the morphology of biomass chars from different sources switch grass, pine, rice husks, wood, forest product, maize stalk and many other biomass materials [135,136,141,143–145] indicate that char particle size, shape and texture vary considerably, and upon combustion. There is also evidence of a significant change in both particle size and material structure. There is a loss of cell structure in high heating rate biomass chars which results from the melting of the cell structure i.e. occurrence of plastic transformations. During the decomposition there can be a considerable yield of tar (especially for low-K feedstocks) which subsequently decomposes to participate in soot forming reactions and subsequently polymerizes to form additional carbon and also helps to determine the final particle shape and porosity (Fig. 13).

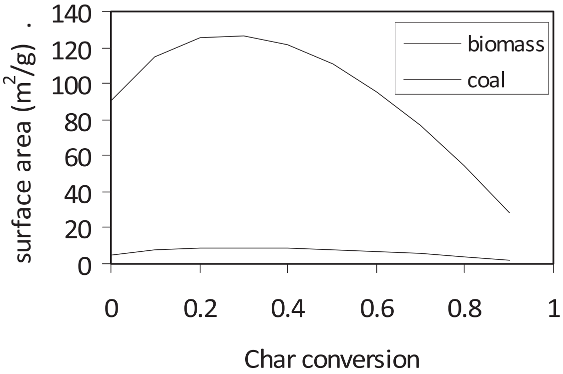


Fig. 13. Estimated variation of surface area for woody biomass using the pore-tree model and using data from [141,142,143,144].

3.5.2. *Char combustion in beds: fixed, moving or fluidised*

In many boilers, such as fixed, moving (or travelling) or fluidised systems, there is combustion of larger char particles. The temperatures of these different types of beds however are approximately the same, about 850–1000 °C, although the temperatures in the combustion region above the bed may be slightly higher. Here the char formed in the first instance contains a significant amount of oxygen, potassium and volatiles, and are, thus more reactive [120,127]. Heating of these low temperature chars results in loss of volatiles [146], which is also marked with a dramatic change in electrical resistivity.

A number of measurements have been made representing char combustion in fixed or fluidised beds. Most of these have been made using TGA type of experiments and mainly directed at the rate of char combustion, although some measurements have been made of the rate of release of other species [147–150]. In general, with some well-characterised fuels, such as wood with a known potassium content, it is possible to make a prediction of the burning rates under fluidised bed conditions, but this is not always the case in fixed beds. Thus, Lang and Hurt [145] presented reactivity measurements of chars formed at 700–1000 °C including char from tyres, wood, agricultural residues, and refuse-derived fuel. Here, it was found that standard reactivities at 500 °C in air varied considerably and correlated poorly with the organic elemental composition or char surface area. Di Blasi and co-workers [105,140] studied wheat straw, olive husks and grape residue, all high potassium-containing, in the low temperature kinetically controlled regime (about 600 °C) and found the reactivities on a mass basis increase with conversion initially and then decreased and then again increased.

A one-step global model has been used by a number of groups to describe the mass loss curves with conversion-dependent parameters [eg, 141,148,149]. Kinetic data that have been obtained has been compiled by Di Blasi [140], some of which is included in Fig. 10. Even, for small particles it is clear that there are many different influences on char combustion rates (potassium and sodium contents, porosity, surface areas, tar release, and the interplay of these factors).

Consequently, in the case of large particles, it may be concluded that it is very difficult at present to predict exactly *a priori* the rate of combustion of chars. In addition it is only possible to predict the amount of fragmented char micro-particles in an empirical way. This makes calculations of the emission of fragmented char particles very challenging indeed. Since this is of importance in small combustion systems where burnout of these particles cannot take place it is clear that further research is needed in this area.

The rates of combustion of chars containing non-metallic trace pollutants such as nitrogen and sulphur are assumed to be the same as that for the pure biochars. In the case of nitrogen the assumption of constant N/C often holds but it is not always the case [40]. The behaviour of the metals, especially potassium, is much more complex because the combustion rate may be catalysed as previously discussed. The rate of release can often depend upon the chemical nature of the compounds involved, for instance whether it is KOH or KCl.

4. Chemical mechanisms for the formation of trace pollutants

The previous section has outlined the current knowledge regarding biomass and introduced routes to the formation of the major pollutants CO and the incompletely combusted hydrocarbon based pollutants. The nature of the pollutants produced depends on the form of combustion. Generally large combustion units, with carefully monitored combustion control form low levels of pollutants whereas small units with poor mixing, poor instrumentation and no control tends to result in high levels of pollutants. The pathways leading to the formation of pollutants have already been shown in Fig. 7. Smoke is a consequence of secondary reactions arising from unburned volatiles. The trace species, S, Cl, K and Na can influence the course of combustion as already described but can have an impact on soot and PAH formation, and can influence the emissions of SO_2, HCl and aerosols [148].

Extensive studies have been made of pollutants emitted from small stoves, large domestic and commercial rigs, power plant involving fluidised beds or pf combustion, and co-firing of biomass and coal and these are outlined in the following sections.

4.1. *Smoke and unburned hydrocarbons*

A general mechanism for the organic components in smoke formation is set out in Fig. 14. Smoke consists of a number of components: carbonaceous soot; inorganic, organic, and aqueous aerosols; CO, VOC and PAH; and also small particles of char (unburned fuel/carbon) from the disintegrating fuel particles and entrained in the hot gases and vapours. There are approaches for modelling the formation of carbonaceous soot, aerosols, CO, VOC, and PAH, but modelling the entrainment of unburned fuel/char, which can be a significant component, is extremely difficult. Fortunately because the particle sizes of the latter are larger than those nucleated from the gas phase it is more readily controlled. The inorganic aerosols are discussed later.

Fig. 14 summarises the routes to organic emissions and soot emission from biomass combustion. Soot can be produced during the combustion of biomass and the extent of the soot and its nature is a function of the combustion conditions and the post-flame temperature-time history. During the combustion of the biomass both pyrolysis and oxidative pyrolysis of the biomass components occurs with the release of tars and vapours. In most applications, the particles are large and all the combustion processes take place as a thermal wave through the particle either as a self-sustaining flame front, as smouldering or as pyrolysis. The initial products obtained are a function of the composition of the biomass, the water content and the stoichiometry.

The species given in Fig. 14 are caused by incomplete combustion and hence the level of the emissions can be controlled by the design features ensuring mixing of the fuel and air [149]. If the temperature is low (below ~ 700 °C) as might be the case in small cook stoves and units based on smouldering combustion, and there is poor mixing, then compounds in the bottom half of Fig. 14 dominate in the smoke. At higher temperature (above ~ 900 °C) which would be the case in larger domestic combustors and industrial furnaces, emissions of pyrolysis products decrease and compounds in the top half of Fig. 14 become more dominant. In the combustion of hydrocarbons the HACA mechanism would dominate where acetylene formed in the early part of the combustion zone would first form benzene, then polycyclic aromatic compounds which would go on to form soot. References to HACA and related mechanisms leading to the formation of soot in hot flames are given in [117]). In this mechanism, which stands for 'H-Abstraction–C_2H_2–Addition' the key growth species is acetylene and the flame temperature has to be hot enough to form acetylene. The acetylene forms benzene in the first instance which goes on to successively produce increasingly large PAH species ultimately leading to soot particles. Overall the reaction can be represented by

$$Ai + H = Ai\cdot + H_2 \qquad \text{(viii)}$$

$$Ai\cdot + C_2H_2 = AiC_2H + H \text{ etc} \qquad \text{(ix)}$$

In the case of biomass combustion additional routes involving aromatic species and reactive intermediates such as cyclopentadiene derived from the lignin come into play, but this depends on the amount of lignin in the biomass and the reaction conditions [117–122]. Emissions of soot and the precursor aromatic and PAH compounds are compounded by poor mixing where pockets of unburned vapours may exit the combustion system. A considerable number of studies have been made on emission of smoke and other pollutants, particularly of fixed bed grate combustors with small or medium thermal capacity, and also from moving bed combustors and suspension or pf combustion. General guides are available via compilations of emission factors [eg [44,150]]. Similarly, extensive studies have been made of the PAH and dioxin emissions [19,151].

A considerable body of information exists on the related process of smoke from the combustion of hydrocarbon fuels, but whilst there are some similarities there are fundamental differences. The

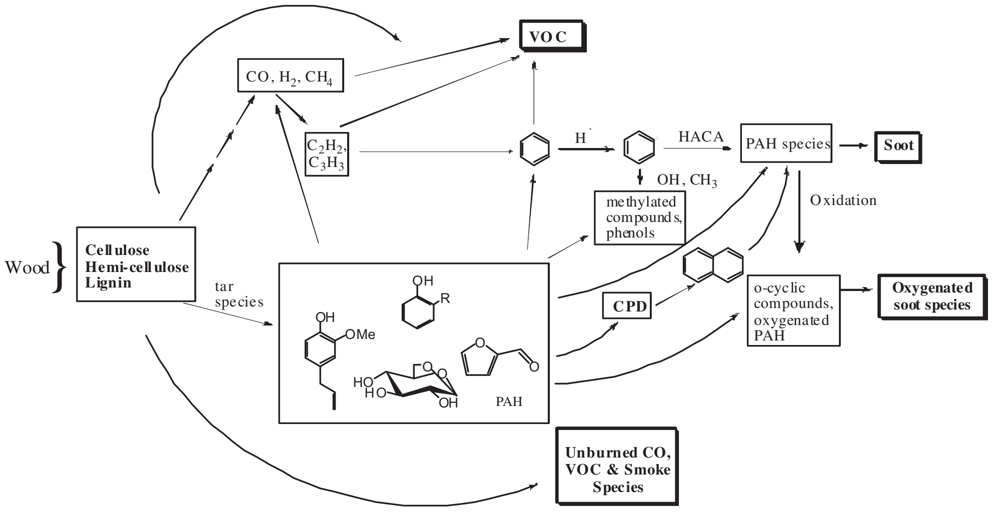


Fig. 14. Pathways leading to smoke and unburned volatiles. [based on [117,118]].

particulate from biomass consists of large polyaromatic hydrocarbons, oxygenated aromatic compounds and pyrolytic PAH material derived from these compounds, residual unburned char particles and products that are condensed on the particulates [19,20,117,118]. The nature of the resultant aerosols depends on the way in which they are formed and on their time-temperature history as they emerge from the combustion zone through the flue and are emitted into the atmosphere [21,22].

4.2. NOx and nitroso compounds

NOx production during the combustion of fossil fuels has been studied extensively [149], and in the case of coal combustion arises from three main mechanisms: thermal-NOx from high temperature oxidation of atmospheric N_2, prompt-NOx from the reaction of fuel-derived radicals with atmospheric N_2, and fuel-NOx from oxidation of nitrogen which is chemically bound in the fuel [152–155]. The mechanisms of the first two routes are well known [149], the former being dependent on the reaction of oxygen atoms with molecular nitrogen and the latter the reaction of CHi species with molecular nitrogen. Their contribution usually only a small percentage ($<30\%$) to the total amount of NOx produced in most biomass combustion systems, even with those with long residence times (>1 s). The majority of the NOx is produced from the fuel-bound nitrogen which in biomass is present as inorganic nitrate and ammonium ion, amino compounds (includes proteinaceous fraction), heterocyclic purines, pyrimidines and pyrroles. Two examples of these compounds are given in Fig. 15 (a), one is a linear protein and the second is a cyclic compound. On pyrolysis the former tends to produce NH_3 and the latter to produce HCN [152,153,155].

Fuel-nitrogen containing species will be released in combustion both during the devolatilisation and in the char combustion stage. In many boilers, NOx formation during the volatile combustion can be controlled by stoichiometry control, whereas NOx formation from char combustion is more difficult to control. Thus, an important factor is the nitrogen partitioning between the volatiles and char [40]. It can be determined experimentally, for example in [40], or by devolatilisation codes (see Section 3.4), although this method is not very accurate at present for biomass compounds.

There is variability both in total N-content and in composition between biomass types as shown in Table 2. Indeed there are difficulties in the accurate measurement of the amount of nitrogen in biomass because of their small quantities and interference effects, and errors here are result in uncertainty in the calculation of the amount of NOx produced. Natural senescence leads to a lower N content as the N is remobilised to the roots or rhizomes. Nitrogen oxide emissions can therefore be controlled, to a certain extent, by an informed choice of the biomass (e.g. harvest time), and/or pre-treatments with a target of minimising heterocyclic-N compounds. Experiments show [40,154] that the heating rate (and final temperature) and particle size have substantial effects on the primary N-conversion and on the secondary reactions influencing the formation of NH_3, HCN and HNCO and their interconversion. However, it should be noted that the products obtained by pyrolysis experiments in an inert atmosphere are not quite the same as those under oxidising conditions. This is a well-known feature in droplet combustion because of diffusion of

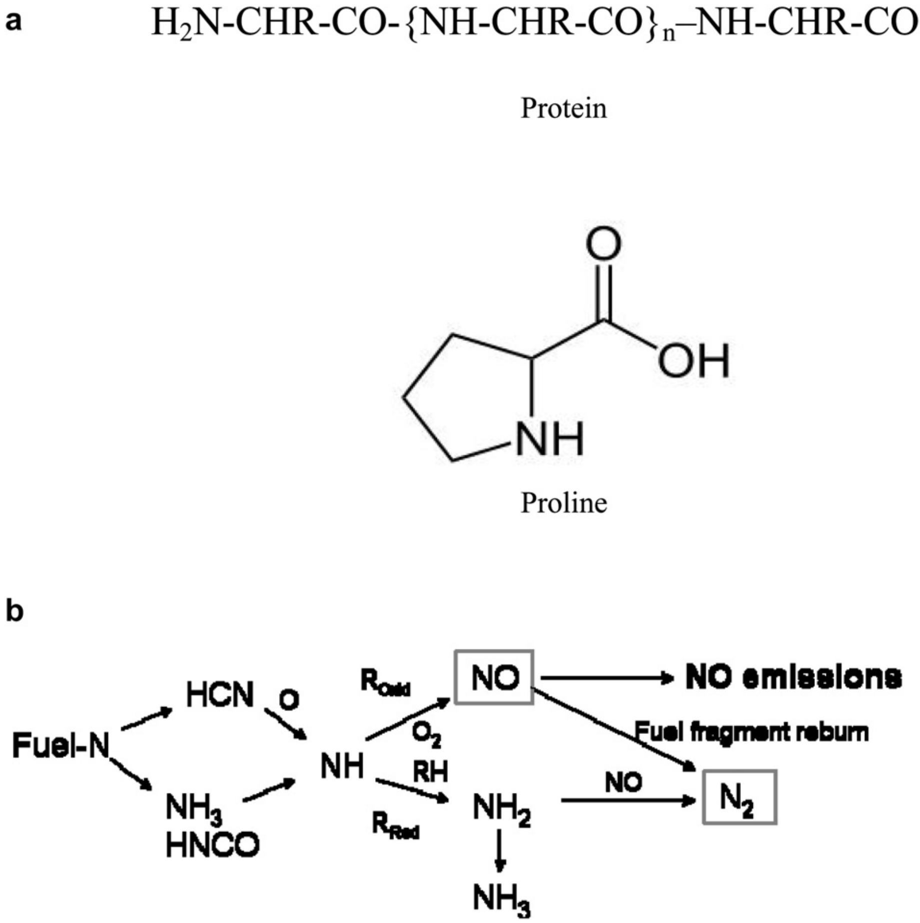


Fig. 15. (a) Examples of biomass-nitrogen types, a linear protein and cyclic N-compound, and (b) NOx formation pathways from fuel-nitrogen.

a small amount of oxygen from the surrounding atmosphere through the flame zone to the droplet surface. It will not change the composition of the bulk species diffusing from the surface but can influence trace species such as HCN and NH_3. Thus, the presence of O_2 promotes the yields of HCN and HNCO from biomass. [155].

The mechanism of gas phase formation of NO from the fuel-nitrogen compounds in the volatile compounds is set out in Fig. 15(b). The composition of the fuel-nitrogen species and the surrounding biomass structure are reflected in the N/C, N/H and N/O ratios. Thus different types of fuels produce different initial species although the evidence at present is somewhat conflicting since the ratio of HCN to NH_3 depends on the temperature and possibly on the mineral content, especially potassium content [153]. HCN/NH_3 and HNCO/HCN ratios increase with the increase in the fuel H/N ratio. Both HCN and HNCO are the main N-containing gases for rice straw, while NH_3 and HCN are the main N-containing gases for wheat straw [153]. Stubenberger et al. [154] indicate that the fuel-N is all converted to NH_3 except in the case of wood. A number of studies have been made of the decomposition of model compounds, poly-L-leucine [152] and the co-pyrolysis of biomass components and amino acids. [155]. The results indicate the importance of the interaction which influences the composition of the pyrolysis gases and the char.

The oxidation of HCN and NH_3 can be described [156] in a generic form by equations (x) to (xiii) given below:

$HCN + O_2 \rightarrow NO +$	(x)
$HCN + NO \rightarrow N_2 +$	(xi)
$NH_3 + O_2 \rightarrow NO +$	(xii)
$NH_3 + NO \rightarrow N_2 +$	(xiii)

The detailed reaction mechanism consists of hundreds of reaction steps and the current status of these together an analysis of the simplified overall global reactions has been summarised by Hansen and Glarborg [156]. The most widely used correlations to describe the reaction of HCN and ammonia are the De Soete expressions employed in, for example, the ANSYS Fluent CFD models [99]. These correlations do not work well in rich conditions and in this more recent work [156] correlations for the prediction of NO formation from both HCN and NH_3 were derived for volatile compositions representative of solid fuels for temperatures of 1200–2000 K.

NO is also produced from the oxidation of the char-N and knowledge of the N-content of the char is important [40]. The formation of NO and N_2O from char is complex and will depend on the nitrogen functionality in the char although the mechanism is probably similar to that for coal char. There have been many studies of the formation of NO from coal char nitrogen and there is recent evidence that HCN is the main precursor for NO at temperatures of 1170–1570 K [157], a temperature range which is applicable to bed and pf combustion. No similar study has yet been made for biomass char but it may be expected that biochars produced at high temperatures are similar to coal char. However biochars produced at lower temperature, say in fixed beds which may contain a higher oxygen content in the carbon matrix, may form NO and N_2O directly from the char matrix [139].

N_2O formation can also take place, especially in fluid bed combustion, by the reduction of the initially formed NO by the char particles [158]. It is possible that the more oxygenated char will yield higher N_2O upon combustion, and thus this may be even more important for biomass combustion in fixed and fluid beds.

Nitroso compounds can only be formed when there is unburned hydrocarbon present, when NO can interact with hydrocarbon free radicals, but normally this can only take place in unconfined flames and fires.

4.3. The release of SOx and Cl compounds

Sulphur is a major plant nutrient and is necessary for the metabolism of plants. Normally it is taken up from the soil in the sulphate form although it can be assimilated from sulphur dioxide in the air, and the leaves have the highest content. Biomass tends to contain only small amounts of sulphur (0.1–0.5% dry plant matter, which is small compared with most coals) and the substitution of coal by biomass in co-firing is usually advantageous in this respect, although it can play a role in aerosol formation.

The concentration of chlorine in biomass ranges from 0.2 to 2% and the high concentrations found in some straws is a major combustion problem. F is also present at low concentrations (typically > 0.001 wt%). Both Cl and S are present both as organo-compounds, but mainly as inorganic salts (particularly potassium salts) in solution in the xylem and phloem. Both chlorine and sulphur are released partly during devolatilisation, and the more refractory salts are retained and released during char combustion [158,159,160,161,162,163,164]. Chlorine can react with metals such as K and Na, forming vapours and then aerosols during the cooling processes. This also leads to deposits on the furnace walls. Chlorine (as HCl) can also react with organic constituents producing dioxins [151]. The various reaction steps are given in Fig. 16.

The release of metals from the char is by sublimation or evaporation of the oxides, hydroxides or chlorides. Thus the emission of KCl has an apparent activation energy close to that of the sublimation energy of KCl of 211 kJ/mol [158].

Apart from the aerosols dioxins can be formed. The formation of dioxins is complex, and in the early days of co-firing there was concern that the addition of the Cl-containing biomass would cause environmental problems. Essentially any hydrocarbons present in the hotter regions of flue gases can rearrange to give initially benzene and then phenols under oxidising circumstances. These readily form phenoxy radicals and these can combine to give dioxin precursors. Chlorination catalysed by metals in the fly ash can give polychlorinated dioxins. Since biomass flue gases, especially straw, contains HCl, this is a potential problem [165]. However as long as combustion is complete, so decreasing the amount of C/H species in the flue gases then the atmospheric environmental problem is minimised.

4.4. Metals and particulate metal aerosols

Biomass contains metals of which the most important is potassium, which varies from several thousand ppm in energy crops to a few wt% (dry basis) in certain agricultural residues. On combustion these are released, forming inorganic species which can condense and are deposited in the furnace causing slagging, fouling and corrosion, but a small quantity can be released into the atmosphere as aerosols, as illustrated in Fig. 16. This former aspect is a major topic considered in many reviews and will only be considered in outline here where it impacts on the environmental issues.

As far as emissions are concerned the various metal components are released [12,159,160,161,162,163,164,165,166] and interact in the gas phase with sufficient reaction time available to come to equilibrium, the products thus depend on the temperature. The most important species present would be K, Na and Ca compounds, the volatile metals Pb and Zn and S and P as indicated in Fig. 16, together with other trace metals such as Cr, Mn, Fe, Co, Ni, Cu, Ga and As. Their composition would depend on the nature of the biomass and mainly on the resultant amounts of K, Cl, HCl, $SO_2$and SO_3 and their interaction, and on the temperature, as shown in Fig. 17. These products on reaching cooler parts of the combustion chamber, condense and some are emitted as aerosols of alkali

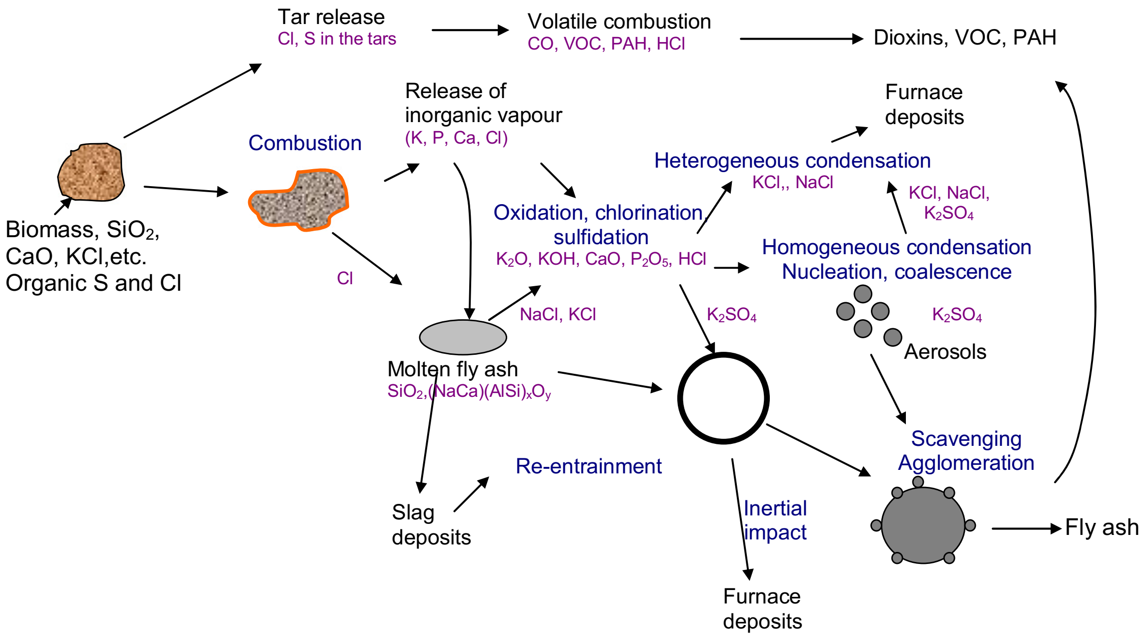


Fig. 16. Aerosol, deposits and pollutant formation pathways for K, Cl and S compounds. Adapted from [165].

sulphate or alkali chloridein particles with sizes less than 1 μm. These fine particles are enriched in most of these elements with respect to the bulk fly ash due to vaporization and subsequent condensation.

Detailed studies have been made of the emissions from the combustion of wood under fixed bed conditions at 500–1150 °C [162], from wood combustion on a travelling grate [163] and from small particles of olive residue and three different woods in an entrained reactor simulating pf combustion [164]. Jimenez and Ballester [164] demonstrated a general rule that that biomass forms fine particles of alkali sulphates and chlorides in the range of 0.1 μm–0.5 μm together with coarser particles (about 1 μm from the char and high melting point ashes). The combustion of Si-containing products such as rice husks adds a further complication [141] because of the formation of silica particles that may be emitted or deposited.

Most of the alkali metal compounds are deposited in the combustion chamber, in which case it is necessary to have an understanding of the transformations that take place in the formation of the ash. This is particularly complex if silica is one of the products. Condensed alkali metal compounds form sticky surfaces onto which ash particles adhere producing deposits, and their effect is dependent on the furnace type. In large furnaces using pulverised fuel or travelling grate combustion stations with a high furnace temperature much of the deposition occurs on the superheaters. In fluidised beds, bed agglomeration can take place. In grate units, both corrosion and deposits are observed depending on the conditions. These deposits can break off giving larger particulates in the flue gases which can readily be captured by pollution control equipment [161].

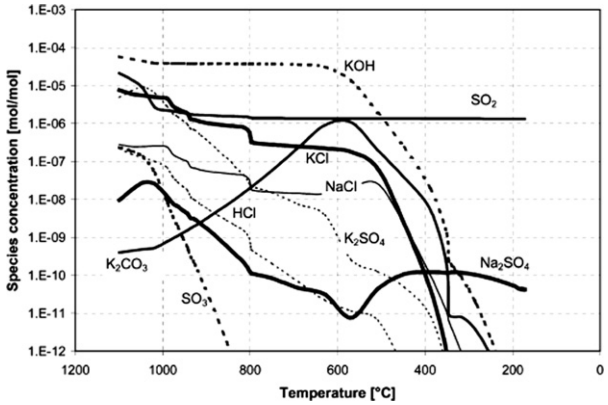


Fig. 17. Equilibrium gas phase species relevant for aerosol formation during beech combustion: from ref [163] with permission.

Additives can be used to control boiler deposit problems arising from the deposition of alkali metals. But the way this is undertaken differs from that with coal. For example, if calcium compounds are added to remove sulphur, this would influence the interplay between the S and Cl compounds and would result in the formation of increased KCl, which is not the desired outcome. However, whatever action is taken impinges on the emissions of both gases and particulates.

4.5. Emissions from different types of combustion systems

The emissions from all combustion devices consist of gases, particulates and the residual ash. The control of gaseous pollutants involves the interplay between achieving complete combustion to minimise unburned CO, hydrocarbons and associated products such as carbonaceous smoke (soot) and PAH, and on the other hand minimising NOx by reducing the temperature and residence time [17,166]. The disposal or utilisation of ash from the bottom of the furnace or from particulate collection devices presents another pollution issue [166,167] but this aspect is not considered here.

The emissions are largely determined by the size of the combustion unit, and the legislation which is applicable reflects the effect of size, although this varies from country to country. In the EU new combustion plant larger than 300MW$_{th}$ are limited to an emission of 200 mg/Nm^3 at 6% O_2 for NOx, 20 mg/Nm^3 for particles, and 200 mg/Nm^3 for SO_2. These emission limits have become increasingly stringent over time. Similar limits apply in the USA, Japan and other major countries. Proposed limits in the EU will be lower for NOx. For smaller combustion plant the emission limits are higher at present, and in the case of plant below 500 kW the solids emission may be five times as high or not legislated at all. A considerable amount of information is available on emission factors [44,152] and whilst the NOx may be similar to that for oil fired burners it is much higher than gas fired units. Smoke emissions are high and consequently there is a need to reduce these levels.

Typical emission values are set out in Table 3. The sources are Ref. [23,150,168–177]. They cover a range of combustion devices, from small village stoves through to large power stations. The choice of fuel is important, although wood is the major fuel used. Low quality fuels such as animal dung can contain high levels of fuel-N and produce smoke.

4.5.1. Fixed and moving bed combustors

Cooking stoves, small heating and small commercial or residential CHP plants are a problem in regard to particle emission, especially in small-scale plants with a nominal capacity smaller than 1 MW_{th}, where the installation of efficient aerosol precipitation devices is too expensive to be economic. Small combustion units with a short residence time and poor mixing of the fuel and air tend to be the major source of particulates [14,15,164–167]. Small biomass units are widely used in developing countries and considerable efforts have been made to reduce pollution especially when these are used indoors. Usually this involves the improvement of mixing or reduction in heat loss which, while increasing the combustion temperature, has the unfortunate side-effect of increasing the NOx as a consequence. Any unburned hydrocarbons and CO in the combustion gases ultimately form (or reform) CH_4 [15]. An extensive literature exists in relation to indoor heating by biomass, a method widely used in developing countries and the health hazards are well documented [164–172].

While small biomass cooking stoves present serious emission problems there are still problems with advanced combustion chamber designs. With these, although NO levels are lower than for oil fired equipment they are higher than for natural gas fired units. Particulate emission is also a much more general problem since biomass combustion has been shown to be still a source of particle emissions, especially in countries that extensively use biomass. Often emission levels are above 50 mg/m^3 (at 11% O_2). The majority of the particulates are smaller than 10 μm (PM10) with a high proportion of submicron particles (PM1). This problem is recognized by environmental pollution agencies in many countries and new and more stringent regulations limiting the emissions are expected to be implemented in the near future. At present there are no common international standards for emission control from small-scale biomass burning - national or even regional emission standards are used. In this context emission measurement programmes were carried out at small-scale combustion units and domestic stoves in Germany (6–450 kW) to determine the fine particles [172]. Data for PM10 obtained in this way are plotted in Fig. 18 against appliance size and it is clear the effect of fuel, fuel type, whether chips or pellets of wood, and appliance size are important. For the type of appliance shown in Fig. 18 wood chip is the best fuel. Generally, the larger the combustion chamber the longer the reaction time available, which in turn permits the burnout of the carbonaceous part of the particulate. Thus the particulate from the larger units consists of submicron particles of inorganic material.

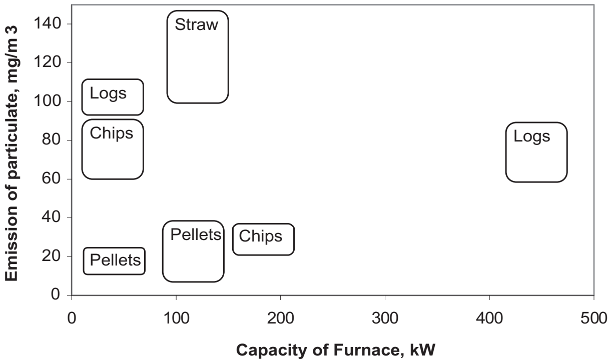


Fig. 18. PM10 Plotted against appliance thermal capacity, based on ref [172].

4.5.2. Large combustors: fluid beds; PF combustion and co-firing

Large combustion plant is normally equipped with pollution control units and so the final flue gas emissions are to a large extent controlled by that equipment. Generally plant up to about 20MW_e would have particulate control equipment, bag filters or electrostatic precipitators. Large plant over 50 MW_e would have NOx or SOx control equipment, and so the flue gas loadings at the end of the combustion chamber would be treated prior to release into the atmosphere. Typical emissions for NOx are shown in Table 3 [176,177]. The UK/EU limit is currently 500 mg/Nm^3, 6% O_2, but will be reduced by 2016 to 200 mg/Nm^3 at 6% O_2. Similar reductions are also required in US and Japan, and so considerable reduction of NOx is required in the next decade. Thus new power plants are being constructed globally which incorporate control equipment for NOx, SOx and particulate removal largely based on coal combustion plant experience. The main issue is whether these plants can accommodate the fine particulates produced from biomass.

Obviously the effect of the biomass fuel has to be integrated with these pollution control measures [53,179]. Extensive studies on co-firing have been made [e.g. [39,42,52–54,174,179]]. Spliethoff and Hein [179] have shown that the effect of co-combustion with biomass has a beneficial effect on emissions in pulverized fuel furnaces. Since in most cases biomass contains considerably less sulphur than coal, an increasing biomass share in the thermal input makes the SO_2 emissions decrease proportionally. SO_2 can also partly be captured in the ash by the alkaline–earth fractions of the biomass ash. Due to the high volatile content of the biomass, low

Table 3
Typical emission levels from the combustion of biomass for various sources. Ratings are given in thermal capacity. Average values are given for the whole firing cycle.

Type of unit	Village Cook stove	Residential boiler, 2–10 kW	Pellet stoves, fixed grate 2–25 kW_{th}	Fixed Grate[a] 20 kW–2.5 MW_{th}	Travelling grate[a] 150 kW–15 MW_{th}	Fluid bed[a] 100 MW_{th}	Co-firing: Coal/biomass[a] 1 GW_{th}
Fuel	Wood	Wood chips, or miscanthus	Wood pellets	Most biomass	Straw	Most biomass	Most biomass
NOx mg/Nm^3-depends on fuel-N content	100–500	100–500	100–500	150–400	150	150	250
Particulate mg/Nm^3	5000	20–100	20	1	1	5	15
Hydrocarbons mg/Nm^3	100	10	10	10	10	15	0.1
CO mg/Nm^3	250–900	250	200	130	150	5	100
Ref O_2	11	6	11	11	11	11	6

[a] Assumes pollution control equipment fitted.

NO emissions can be achieved both by air staging, over-fire air and by reburning in the way used for pulverized coal fired equipment [38]. Reburn can be undertaken using pulverized biomass but the larger particle size presents a problem compared with pulverized coal or natural gas.

The amount of UBC varies depending on the size of the particles - large/wet particles are incompletely combusted and result in increased UBC. Since it economic to use larger wet, or at least undried, particles of fuel, it is desirable to be able to determine the optimum size for combustion. This applies not only to pf combustion but to all biomass applications.

4.5.3. *Very large-scale combustion: wild fires*

The largest scale of biomass combustion arises from uncontrolled forests fires and grass and controlled waste agricultural burning and land clearing. This contributes about 2500TgC per annum although it varies greatly on a year-by-year basis. This, together with biomass burning for cooking and heating, is a major contributor of particles in the atmosphere [20,22,180,182,183] although other pollutants such as CO and NOx are also formed and can be important.

The relative contribution of biomass combustion emissions from both open and domestic sources to the global annual emission for CO is about 25%, for NOx about 18%, for non-methane organic compounds (NMVOC) about 18% and for methane about 6% (IPCC, 2001 as cited by ref 153). The vast majority of these emissions occur in tropical regions and especially Africa. Some information is available for other regions. Thus, in Europe (which is about 10% of the total emissions) the impact is often severe locally in the short term e.g. from recent fires in Greece and Portugal. According to the CORINAIR-1990 inventory for Europe, forest fires contribute 0.2% to the emissions of NOx, 0.5% to the emissions of non-methane volatile organic compounds, 0.2% to the emissions of CH_4, 1.9% to the emissions of CO, 1.2% to the emissions N_2O, and 0.1% to the emissions of NH_3 in Europe [44]. For short periods of time the contribution for these fires is comparable to the anthropogenic emission with significant effects on the solar radiation properties in these regions.

Overall the pollution effects at ground level are usually small (unless the source is very close) and variable and the main effects are to the climate which are discussed later in Section 6.2.

5. Modelling pollutant formation

The modelling of biomass has followed that used for coal combustion. In the latter case, considerable attention has been directed to the combustion of pulverised coal, which is the major industrial use of coal, and much less attention directed to fluidised bed combustion and fixed bed combustion. This is the same order of difficulty in modelling pollutant formation. In the past much more attention has been directed to modelling the gases, NO and CO than to the particulates.

Biomass combustion can be modelled by the following five main tasks: (i) Gas phase flow and volatile combustion predictions, including pollutant predictions; (ii) Particle fluid dynamics and inter-phase heat/mass transfer; (iii) Devolatilisation modelling (discussed in Section 3.3) and combustion of the gases released (Section 3.4); (iv) Char combustion and fragmentation modelling (Section 3.5); (v) Pollutant release including gases, coarse and fine particles (4.0). In addition there are three interconnected aspects of CFD modelling that have to be considered: (i) Conservation equations - which track the reactants, the products and heat release rates; (ii) Heat transfer in the furnace enclosure which determines the temperature field; and (iii) aerodynamics that determine the flow and residence times. Correct prediction of the flow and temperature fields is important especially for NOx estimation. The choice of the turbulent models influences the prediction of the emission of the unburned gaseous species since much of this material results from turbulent eddies containing incompletely reacted products. The use of the LES (large eddy simulation) turbulence model as opposed to RANS (Reynolds-Averaged Navier Stokes) may be important in these types of predictions. The key equations are those for conservation, mass, energy and species which have been set out in many text books, e.g. [184]. The main features of the chemical mechanisms have been set out in Sections 3 and 4 and the way they are interconnected is set out in Fig. 19. Again it is possible to use large reaction mechanisms with hundreds of reactions but for CFD applications these are usually reduced.

Some aspects of modelling biomass combustion are relatively easily undertaken but those dealing with fixed or fluid beds are extremely complex because of the difficulty of including the fragmentation or attrition of the solid phase material. In the next section the outcomes of some major examples of modelling of pollutant formation will be considered.

5.1. *Modelling fixed or moving bed combustion*

Much of the early work on modelling pollutant formation from grate (fixed bed) has been summarized by Saastamoinen and Taipale [177]. The models present a number of problems because, whilst the gaseous combustion occurring in the furnace chamber above the surface of the bed is relatively easy to simulate, this is not

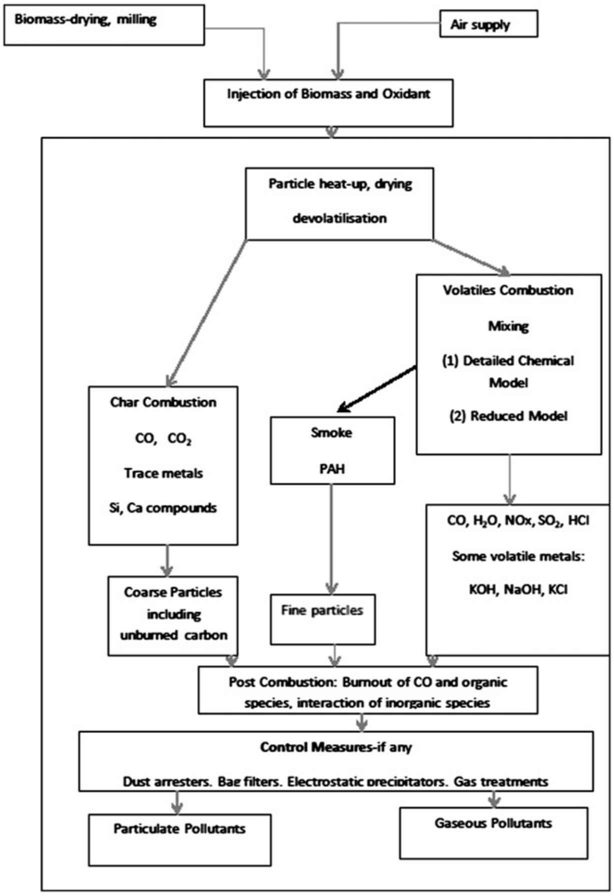

Biomass-drying, milling
Air supply
Injection of Biomass and Oxidant
Particle heat-up, drying devolatilisation
Volatiles Combustion
Mixing
(1) Detailed Chemical Model
(2) Reduced Model
Char Combustion
CO, CO_2
Trace metals
Si, Ca compounds
Smoke
PAH
CO, H_2O, NOx, SO_2, HCl
Some volatile metals:
KOH, NaOH, KCl
Coarse Particles including unburned carbon
Fine particles
Post Combustion: Burnout of CO and organic species, interaction of inorganic species
Control Measures-if any
Dust arresters. Bag filters. Electrostatic precipitators. Gas treatments
Particulate Pollutants
Gaseous Pollutants

Fig. 19. Diagrammatic outline of the reactions involved in the modelling of pollutants from the combustion of biomass.

true of the bed combustion itself. The bed consists of irregular shaped particles where the initial fuel size may be tens or hundreds of millimetres or more, and whilst the term ‘fixed’ is used, combustion is not uniformly continuous and the particles are constantly moving. The fuel is often fed on a batch basis and in addition the bed is not fixed in space and holes can appear through the bed in a random manner, known as ‘channeling’. Moving or travelling grate furnace arrangements are simpler in many respects in that input and movement of the fuel particles in the bed can be treated in a statistical manner, although channeling still occurs. Many of the modelling studies undertaken relate to the heat and mass transfer in the furnace and these are not considered here, but only those relating to pollution formation.

There have been very few modelling studies of pollutants from small village cook stoves. Baskar Dixit [170] and Kausley and Pandit [185] studied flow and heat transfer in cook stoves but not pollutant formation. Ndiema el al [15] investigated the formation of NOx, methane and smoke experimentally in a 1-D plug flow model of a cook stove, and the gaseous pollutants by Chemkin modelling.

A number of studies have been made of larger fixed bed combustors for residential and commercial applications combustion using a variety of fuels [174–177,185–193]. The earlier published modelling studies [e.g. [174,186]] were related to the use of fuels such as wood with an irregular size or briquettes made of sawdust or straw. Later studies were much more general and looked at the influence of the many factors involved such as bed

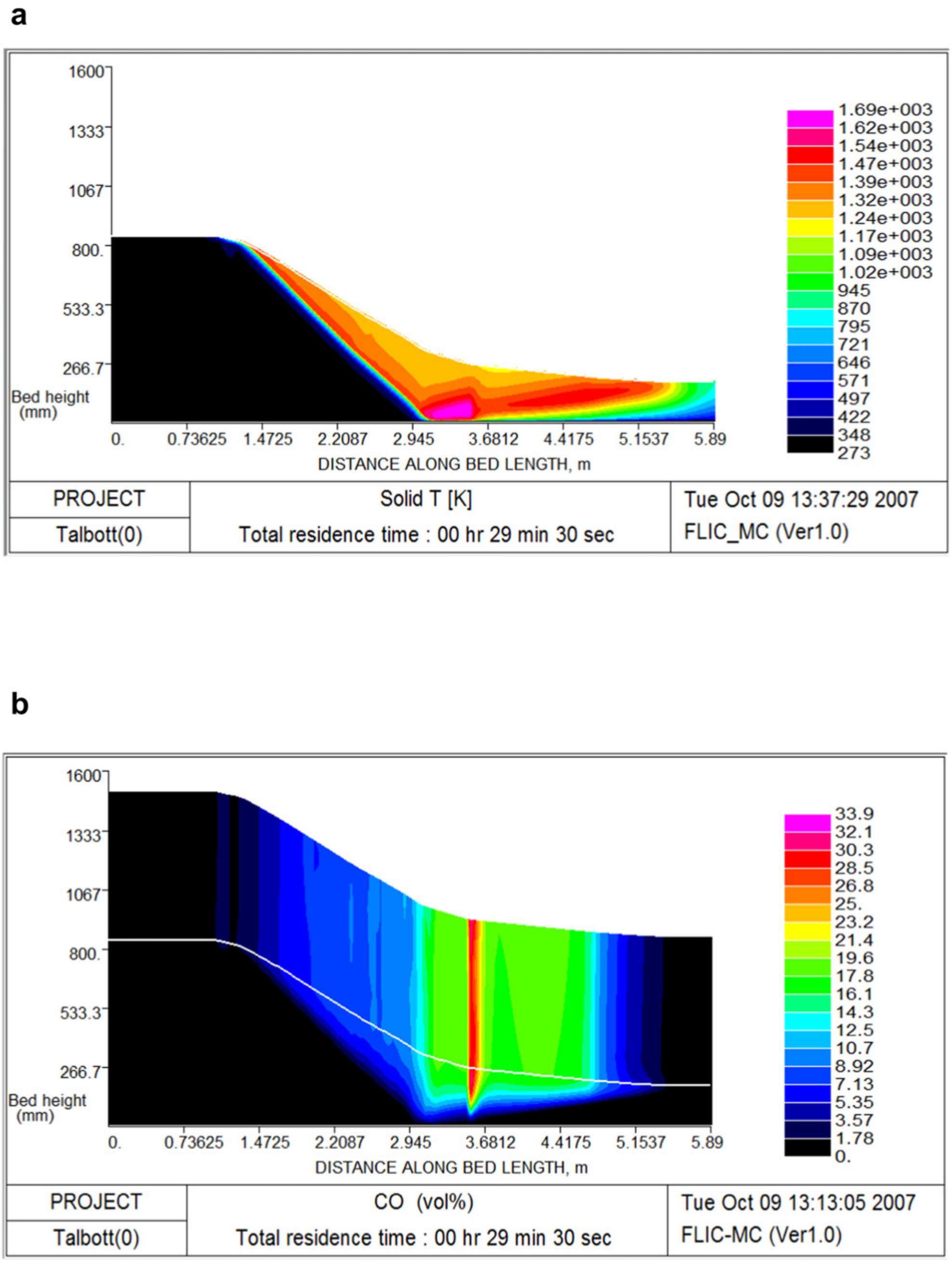


Fig. 20. Modelling moving grate combustion showing (a) the reaction zone and bed combustion, the temperature of the solid bed is in K. (b) The CO concentration (vol%) immediately above the bed, the position of which is shown by the white line, [190].

size, level of moisture, particle size etc. Cylindrical pot furnace studies are useful because of the consistency of the combustion process, and this has been used to investigate NOx formation from several woods and wood pellets [177]. Because of intermittent combustion in practical systems, the complex gas flow, heat transfer and reaction within the bed, many models have concerned efficiency studies or partial modelling of pollutant formation in the combusting gases above the bed [174,175,186,187,188–193].

The introduction of pellet burners in the last decade has simplified these calculations since the fuel is more uniform and combustion much more consistent. Many researchers have carried out simulation studies of biomass combustion for large particles and pellets, for example references [160,162,170,186–188].

Modelling the emission of pollutants from larger thermal capacity (about tens of MW_{th}) grate units follows the same modelling methods, although the gas flows, especially in the injection of secondary air and in the heat exchanger section, are more complex. CFD modelling in these furnaces has been extensively reviewed by Yin et al. [161]. This review shows how little work has been devoted to modelling pollutant formation in biomass combustion, rather attention has been directed to the problems of ash deposition. There are however a number of examples related to both fixed bed and travelling grate combustion. Yang et al. [188–190] simulated packed-bed combustion of biomass particles with size ranging from 5 to 35 mm using the FLIC program which enables a study to be made of combustion in a moving bed. This however would only permit prediction of the release of species (volatiles, CO, NH_3, HCN, KOH and HCl etc.) from the bed and subsequent reaction of these products in the combustion chamber above the bed would have to followed using CFD modelling coupled with an appropriate chemical mechanism. The amounts emitted would be dependent to a large extent on the design of this part of the equipment. A typical computation for a moving grate burning wood is given in Fig. 20 showing the temperature in the bed and the concentration of CO produced.

Whilst many of the studies have been concerned with the major fuels, wood and straw, some papers have considered other biomass materials such as bagasse [193].

5.2. *Modelling fluid bed combustion*

Fluid bed combustion is one of the major methods of utilizing biomass for power generation [42,178,194,195]. A considerable number of plants are installed using a variety of different types of biomass, being particularly suitable for wet agricultural residues. The designs are largely based on those for coal combustion and two types of designs are used, namely bubbling fluidized bed (BFB) and circulating fluidized bed combustors (CFBC), both of which operate with bed temperatures of about 800 °C. The main difference between coal combustion and biomass combustion are the large amount of volatiles produced in the latter case, the greater reactivity, and lower SOx and NOx (and N_2O) emissions. Thus the BFB system is suitable for many applications where neither staged combustion nor in-bed sulphur removal is necessary. It also has the advantage that large particle sizes are possible. Typical plant sizes are 50–100 MW_{th} and, as such, are capable of using major pollution control equipment. Large plant of this type usually has to conform to National Emission Directives and so the level of emission has to be achieved by a combination of the combustion chamber design and the flue gas clean-up plant, which will involve particulate and possibly NOx units. If the K, Cl, Si contents are high, this can lead to submicron emissions. As with most large-scale combustors the amount of NOx and the metals can be determined by modelling [194] or equilibrium modelling [196,197].

5.3. *Pulverised biomass combustion and co-firing*

The modelling of the combustion of small pulverised biomass particles is readily undertaken using CFD methods, although the modelling of the release of the pollutants is much harder. Many studies have been made of pf coal combustion and in a similar way studies have been made of co-firing using a two-component fuel. Since the amount of biomass is often less than 20% thermal the main flame properties such as temperature or velocity are largely determined by the coal combustion processes. The key to the correct prediction of NOx is the correct prediction of the temperature distribution in the furnace especially if staged burners are used.

In large pf-fired, multi-burner furnaces, which use 20% or more biomass overall, the pulverised biomass is injected via individual biomass burners using 100% biomass. There have been only a few such studies studies. Ma et al. [96] have studied the combustion of pulverised wood and determined NOx and unburned carbon in ash in a 1 MW_{th} Combustion Test Facility. A typical computed profile is shown in Fig. 21. The amount of NO computed on the basis that the fuel-N converts to HCN and then reacts to NO using the ANSYSY FLUENT kinetics [99] is 89 ppm, whereas if the NH_3 mechanism is used it is 266 ppm, the former being closer to the experimental results. In the case of most other fuels it is postulated that the latter is the main route, although it has been observed in industry that the injection of biomass in co-firing does not produce the expected reduction in NO associated with ammonia injection [180].

A number of researchers have made CFD studies of the effects of large aspect biomass particles, such as wood and straws since this has an impact on the burn-out rates of the particles [55,95–97]. Such particles have a significant effect on the application of CFD models since the particle flow field may be influenced and the particles may burnout more slowly. Often such particles are represented by spherical particles with the equivalent volume [96] so the burning rates are not quite right. But whether this assumption has much effect on the prediction of pollutant emission remains to be investigated.

6. Pollution control

6.1. *Pollution arising from biomass combustion*

The utilisation of biomass by means of direct combustion processes result in the release of gaseous and particulate pollutants

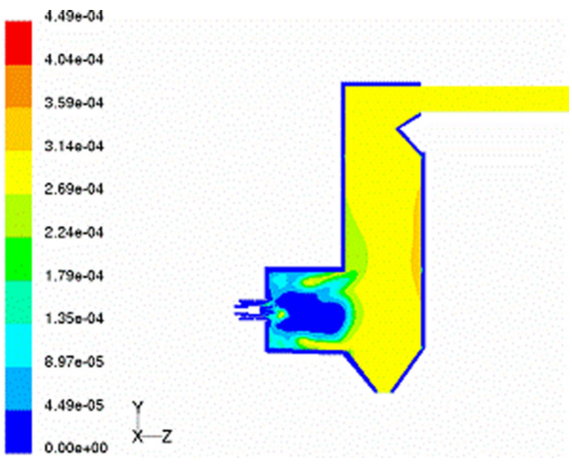


Fig. 21. Modelling NOx formation during the combustion of pulverised wood in a 1 MW_{th}, Combustion Test Facility, based on [96]. The NO concentration is given in mol/mol.

to the atmosphere which can have significant effects if the pollutants emitted are not controlled [198–203]. Because of the move towards the use of solid biomass as a renewable energy source in many countries the future environmental impact has to be considered with care. This is made more difficult because of the diverse pattern of usage. This is on a scale of billions of economically disadvantaged users who use small units for heating and cooking – There are perhaps a billion users of units of about 10kW_{th} for heating, millions of users of units of about 10–100 MW_{th} for industrial and commercial application, and thousands of large plant of about 1–4 GW, users who use co-firing or single fuel applications. It is clear that the most efficient use of biomass is by means of the large combustion units incorporating emission control equipment. Sustainability issues are also better handled with large plant, both from supply and recycling of ash aspects.

In the case of large combustion units, say greater than 100 kW, the size of the unit enables opportunity for the burnout of soot particles either in the combustion chamber or in a secondary combustor. Likewise cyclones and electrostatic precipitators can be used. The major remaining problem are the inorganic aerosols which could be removed by scrubbing or by pre-treatment of the fuel, such as washing or using carefully selected low potassium fuel. Electrostatic precipitators however do not remove all of the submicron or ultra-fine material, nor does washing [204] and research into this area is of major importance.

Many attempts have been made to improve designs of small heaters largely used in the Developing Countries. This involves improving the insulation, thus increasing the combustion temperature, which reduces the smoke and associated hydrocarbons but increases the NOx. These units are so small it is not possible to incorporate staging or particulate removal. The interplay between the C/H/O/N species results in the reformation of methane which is a major problem. A possible reduction in smoke and aerosols can arise by the choice of fuel.

In the case of the larger units, the combustor size permits a longer residence time and more complete burnout of the soot, but the fine particles still remain a problem. At the present time, the levels of NOx and smoke are too high to permit any significant increase in biomass combustion (bio-heat) in any large town in any part of the world. Better combustion arrangements are required. Catalytic emission control units are helpful, as is the use of particle reduction equipment. The choice of pretreated fuels is also useful, in that the reduction of potassium and nitrogen reduces emission, and the use of wood chips results in a fuel that burns more uniformly with a reduced formation of char fragments compared with lump wood.

Large plant has the opportunity of reducing all forms of the pollutants and must be the preferred method of biomass combustion, but control of ultra-fine particles still remain a problem.

6.2. Atmospheric environment and health effects

The presence of biomass pollutants in the air significantly affects atmospheric processes. The effects range from acidification of clouds, rain, and fog, altering cloud microphysical processes in a small scale and mesoscale; and altering the radiation balance of the earth, both directly, by absorbing and scattering incoming solar radiation, and indirectly, by acting as cloud condensation nuclei (CCN) [198–203].

There are large scale effects, resulting from forest and grass fires, especially from particulate and ozone, and these compound problems in regions already having particulate pollution [20,180–183,201,202].

Numerous studies have investigated the characteristics of the particles produced from the influence on climate change. Measurements have been made of smoke (organic carbon, OC and elemental carbon, EC) and of the biological markers and show the considerable effects of these fires. EC relates to elementary, carbonaceous soot whilst OC relates to containing adsorbed incompletely combusted oxygenated products by the mechanism shown in Fig. 14 [20,117,119,180]. The extent of condensation of the oxygenated products on the solid carbon particles varies with the completeness of combustion and the time temperature history of the source and hence differs if emitted say via a hot chimney stack or an open source. There is thus some latitude in the definition of OC and EC.

The issue of fine smoke particles is an issue. For example, in the Western United States it is a significant contribution to regional haze and can have a health impact [181].

7. Conclusions

The combustion of solid biomass already makes a significant contribution to world energy provision. It can play a much greater role than that at present, but ultimately the sustainable biomass resource is limited.

If the increased biomass use is by means of combustion in small units (e.g. for heat or cooking) is increased there could be serious environmental problems arising from particulates, particularly carbonaceous smoke, and from NOx. In larger combustion units where good mixing reduces the carbonaceous element, or it is burned out in the combustion chamber or removed from the flue gases, there remains a potential health problem from submicron inorganic particles. In both cases fuel pre-treatment offers possible advantages. Large combustion units offer the best route to clean combustion because of the advantages of large scale efficient flue gas treatment plant.

The basic features of biomass combustion and resultant pollutant formation are understood but much of the detail is lacking. It seems that if biomass is to be more widely used as a major energy source then a greater understanding of the detailed processes is necessary. This needs to be across all aspects of the combustion and pollution processes. The analogy with the processes occurring in coal combustion is not adequate.

Acknowledgements

We wish to acknowledge useful information from Dr L Darvell, Professor M Chipperfield, Dr D Spracklen, Leeds University; and Dr M Wójtowicz, Advanced Fuel Research, USA. JMJ thanks EPSRC for financial support in the form of an Advanced Research Fellowship.

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